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NUMA NOBUSHIGE

(57) Abstract:

CC(=O)OCC(C)(O)C1=CC=C(C=C1)N2C=CC(=C2)C3=CC=CC=C3
$$\text{CH}_3\text{-C}(\text{OH})(\text{H})\text{-O-CH}_2\text{-CH}_2\text{-N(CH}_3)_2$$

U

functional group selected from carboxyl group, sulfonic acid group and amino group and (D) 0-95 wt. % of other α,β -ethylenic

unsaturated monomers.

* NOTICES *

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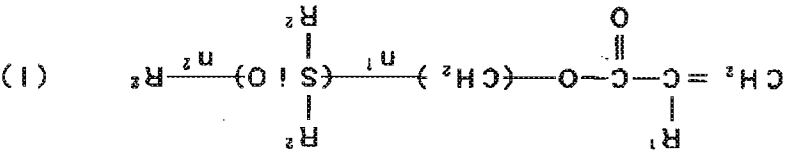
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CLAIMS

[Claim(s)]

[Claim 1](a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by

following structural-formula (i) and (ii), [Formula 1]

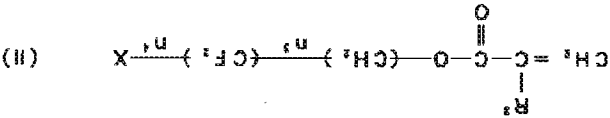


(Among a formula, as for R¹, R² is the same or different in a hydrogen atom or a methyl group, n¹ shows the

integer of 1-10 and n² shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6,

respectively.)

[Formula 2]



(the inside of a formula, and R³ - a hydrogen atom or a methyl group - X shows a hydrogen atom or a fluorine

atom, n³ shows the integer of 1-8, and n⁴ shows the integer of 1-30, respectively.)

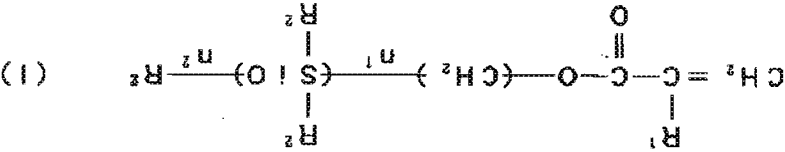
The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta- ethylenic unsaturated monomer 1 to 25 % of the weight, And the copolymer solution or the water dispersion which has the

water repellence carrying out copolymerization of the monomeric mixture which contains alpha in which others

are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer zero to 95% of the weight.

[Claim 2](a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by

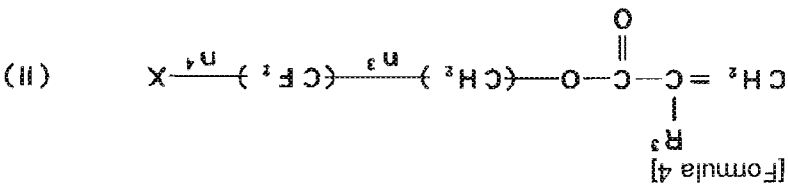
following structural-formula (i) and (ii), [Formula 3]



(Among a formula, as for R¹, R² is the same or different in a hydrogen atom or a methyl group, n¹ shows the

integer of 1-10 and n² shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6,

respectively.)



(the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

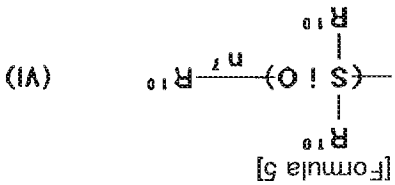
The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta-ethylenic unsaturated monomer 1 to 25 % of the weight, And the monomeric mixture which contains 0 to 95 % of the weight for alpha in which others are [being (d) and] copolymerizable, and beta-ethylenic unsaturated monomer, A manufacturing method of the copolymer solution which has the water repellence which adds water and a neutralizer in the copolymer (A) solution produced by performing a radical polymerization in an organic solvent, and is characterized by aqueous-ization or forming moisture powder, or a water dispersion.

[Claim 3] A manufacturing method of the copolymer solution according to claim 2 in which an organic solvent contains alcohol of the carbon numbers 1-8 10% of the weight or more, or a water dispersion.

[Claim 4] After mixing resin (B) solution which does not contain a water-repellent group in a copolymer (A) solution and in which aqueous-izing or water decentralization is possible, water and a neutralizer are added, and it is a manufacturing method of aqueous-izing, the copolymer solution according to claim 2 or 3 formed into moisture powder, or a water dispersion.

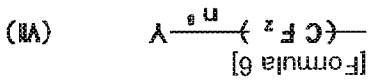
[Claim 5] a copolymer (A) solution — after [or] adding a surface-active agent which has a water-repellent group in a copolymer (A) and a mixed solution of (B) — a manufacturing method of copolymer solution of claims 2 thru/ or 4 aqueous-izing or given in any 1 paragraph which carries out moisture powder, or a water dispersion.

[Claim 6] A manufacturing method of the copolymer solution according to claim 5 whose surface-active agent is what has a water-repellent group shown by following structural-formula (VI), or a water dispersion.



(R^{10} shows a phenyl group or the alkyl group of the carbon numbers 1-6 among a formula, and n^7 shows the integer of 5-200, respectively.)

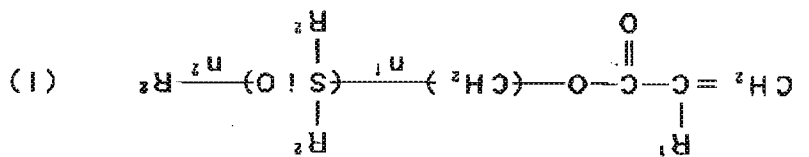
[Claim 7] A manufacturing method of the copolymer solution according to claim 5 whose surface-active agent is what has a water-repellent group shown by following structural-formula (VII), or a water dispersion.



(Y shows a hydrogen atom or a fluorine atom among a formula, and n^8 shows the integer of 1-30, respectively.)

[Claim 8] A manufacturing method of copolymer solution which obtains copolymer solution according to claim 1 or a water dispersion using an emulsion polymerization method, or a water dispersion.

[Claim 9] (a) it is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by following structural-formula (i) and (ii), [Formula 7]

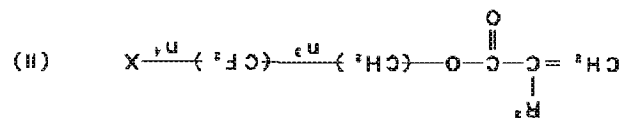


(Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows the

integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6,

respectively.)

[Formula 8]



(the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a hydrogen atom or a fluorine

atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

A monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from a group of a sulfonic group and an amino group, and beta- ethylenic

unsaturated monomer 1 to 25 % of the weight, And a distemper constituent which contains copolymer solution or a water dispersion which has the water repellence which carries out copolymerization of the monomeric mixture which contains alpha in which others are [being (d) and] copolymerizable, and beta- ethylenic unsaturated

monomer zero to 95% of the weight as a vehicle component.

[Claim 10]The distemper constituent according to claim 9 in which a monomeric mixture contains a monomer

which has the (e) carbonyl group one to 30% of the weight.

[Claim 11]The distemper constituent according to claim 10 which contains a hydrazine derivative which has at least two -NH-NH₂ content groups in one molecule as a cross linking agent.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to copolymer solution useful as paint resin which can form the coat which was excellent in water repellence and a water resisting property in detail or a water dispersion, a manufacturing method for the same, and the distemper constituent containing this about the copolymer solution or the water dispersion which has water repellence.

[0002]

[Description of the Prior Art] Although the method of giving water repellence to a dry paint film by mixing in paints the water repellent of low molecular weight which is represented by poly dimethylsiloxane was well known from the former, there was a problem of water repellence falling by temporality. On the other hand, it is possible by taking the method of introducing a water-repellent group into resin like a silicone modification acrylic resin to obtain the high water repellent coating film of water-repellent durability.

[0003] Although aqueosity-ization of such water-repellent resin is strongly called for also from on accident

prevention from the field of the health at the time of air pollution prevention and paint, generally conventional

water-repellent resin has strong hydrophobicity, and aqueous-izing and moisture powder are difficult for it. As a means to solve such a problem, the method of aqueosity-izing by carrying out the emulsion polymerization of the alpha and beta-ethylenic unsaturated monomer to an organopolysiloxane macro monomer is indicated, for

example by JP, 2-150475, A. however, a surface-active agent with hydrophilic nature high in this method -- not

using it -- until it does not obtain but sufficient water repellence is shown -- **** -- it did not result. Although there was also a method of carrying out self-emulsification of the water-repellent resin by hydrophilic functional group introduction of a carboxyl group etc., extremely high resin acid value was needed, and it was not able to be said

to be a desirable method from the waterproof field.

[0004]

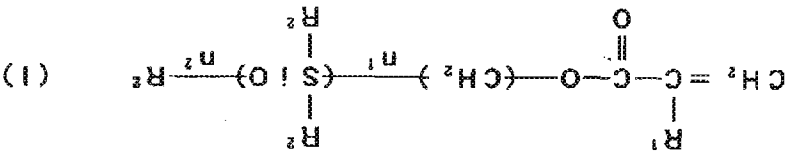
[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned problem should be solved, by making indispensable a monomer which has a monomer and alkoxy silyl groups which give water repellence, this invention persons found out that aqueous resin which can give water repellence and a water

resisting property excellent in a coat was obtained, and reached this invention.

[0005] That is, this invention is 3 to 70 % of the weight about at least one sort of monomers chosen from a

monomer shown by structural-formula (I) and (II) of (a) following, [0006]

[Formula 9]



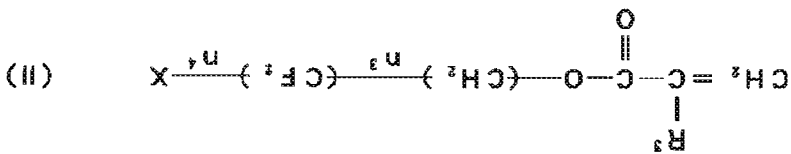
[0007] Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows

the integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers

1-6, respectively.)

[0008]

[Formula 10]



[0009] (the inside of a formula, and R^3 - a hydrogen atom or a methyl group - X shows a hydrogen atom or a

fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has

one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta- ethylenic

unsaturated monomer 1 to 25 % of the weight, And the copolymer solution or the water dispersion which has the

water repellence carrying out copolymerization of the monomeric mixture which contains alpha in which others

are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer zero to 95% of the weight, And

the distemper constituent which contains the manufacturing method and this copolymer solution, or a water

dispersion as a vehicle component is provided.

[0010]

[Embodiment of the invention] At least one sort of monomers (a) chosen from the monomer shown by above

structural-formula (i) and (ii) in this invention, Water repellence is given to a copolymer and any 1 way of the

monomer (a-2) containing the fluoride shown by the monomer (a-1) and the above-mentioned structural-formula

(ii) which have a polysiloxane chain shown by the above-mentioned structural-formula (i), or both can be used.

[0011] In the monomer (a-1) shown by the above-mentioned structural-formula (i), although R^1 is a hydrogen atom

or a methyl group and R^2 is a phenyl group or an alkyl group of the carbon numbers 1-6, there is not necessarily

the necessity that it is mutually the same, n^1 - the integer of 1-10, and n^2 - 5-200 - it is an integer of 15-150

preferably. Since the hydrophilic nature of a copolymer runs short and it becomes poor [water solubility or water

dispersibility] when water repellence with n^2 sufficient by less than five is not acquired but it exceeds 200

conversely, it is not desirable. As an example of this monomer (a-1), "Silaplane FM-0711", "Silaplane FM-0721",

"Silaplane FM-0725" (all are the Chisso Corp. make), etc. are mentioned with a commercial item.

[0012] In the monomer (a-2) shown by the above-mentioned structural-formula (ii), R^3 is a hydrogen atom or a

methyl group, and X is a hydrogen atom or a fluorine atom, n^3 is an integer of 1-8 and n^4 is an integer of 1-30. If

n^4 exceeds 30, since mixing nature with other monomers and copolymeric are inferior, and hydrophilic nature

runs short and it will become poor [water solubility or water dispersibility], it is not desirable. as the example of

this monomer (a-2) - 2, 2, and 2-trifluoroethyl (meta-) acrylate, 2,2,3,3-tetrafluoro propyl (meta) acrylate, 2-

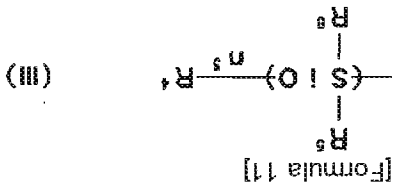
(pentafluoroocetyl) ethyl (meta) acrylate, in commercial items, such as 2-(nonadecafluorodecyl) ethyl (meta)

acrylate, "FAMAC" (made by Nippon Mektron, Ltd.), "screw coat 8FM", "screw coat 17FM" (all are the OSAKA

ORGANIC CHEMICAL INDUSTRY, LTD. make), etc. are mentioned.

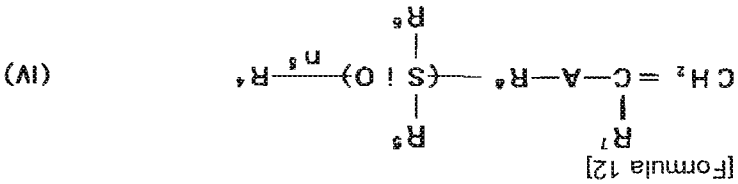
[0013] The monomer (b) which has alkoxy silyl groups in this invention has the alkoxy silyl groups shown by

following structural-formula (iii), [0014]

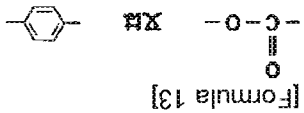


[0015](Among a formula, as for R^5 and R^6 , R^4 is the same or different in the alkyl group of the carbon numbers 1-10, and n^5 shows the integer of 1-4 for a phenyl group, the alkyl group of the carbon numbers 1-6, or the alkoxy group of the carbon numbers 1-10, respectively.) When n^5 is two or more, R^5 comrade and a comrade's R^6 may be the same, or may differ from each other.

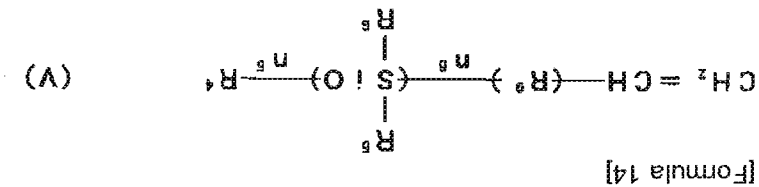
The monomer shown by following structural-formula (IV) and (V) as the example of representation can be mentioned.



[0017](inside of a formula, and A) [0018]



[0019]*****. R^7 shows a hydrogen atom or a methyl group, and R^8 shows the divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6, respectively. R^4 , R^5 , R^6 , and n^5 have the respectively same meaning as the above.

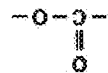


[0021](R^9 shows the divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6 among a formula, and n^6 shows 0 or 1.) R^4 , R^5 , R^6 , and n^5 have the respectively same meaning as the above.

In the above-mentioned structural-formula (IV) and (V), as a divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6 shown by R^8 and R^9 , The alkylene group of a straight chain or the letter of branching, for example, methylene, ethylene, propylene, 1,2-, 1,3- or 2,3-butylene, tetramethylen, ethylethylene, pentamethylene, a hexamethylene group, etc. can be mentioned. As an alkyl group of the carbon numbers 1-6 shown by R^5 and R^6 , The alkyl group of a straight chain or the letter of branching, for example, methyl, ethyl, n-propyl, isopropyl, n-, i-, sec- or tert-butyl, n-pentyl, isopentyl, neopentyl one, n-hexyl, isohexyl, 1-methylpentyl, etc. are mentioned. n-heptyl, 2-ethylhexyl, n-octyl, n-nonyl, n-decyl, etc. other than what was illustrated as an alkyl

group of the carbon numbers 1-6 shown by R^5 and R^6 as an alkyl group of the carbon numbers 1-10 shown by R^4 are mentioned further. As an alkoxy group of the carbon numbers 1-10 shown by R^5 and R^6 , Alkoxy group of straight chain or letter of branching, for example, methoxy, and ethoxy, n -propoxy, isopropoxy, n -, i -, sec - or $tert$ -butoxy, n -pentoxy, isopentoxy, n -hexyloxy, isohexyloxy, n -octyloxy, etc. are mentioned.

[0022]It is A among monomers of the above-mentioned structural-formula (IV). [0023]



[Formula 15]

[0024]Come out and as a certain thing, for example beta-(meth)acryloxy ethoxysilane, gamma-(meta)acryloxypropyl trimethoxysilane, gamma-(meta)acryloxypropyl dimethoxysilane, gamma-(meta)acryloxypropyl methoxysilane, etc. can illustrate suitably.

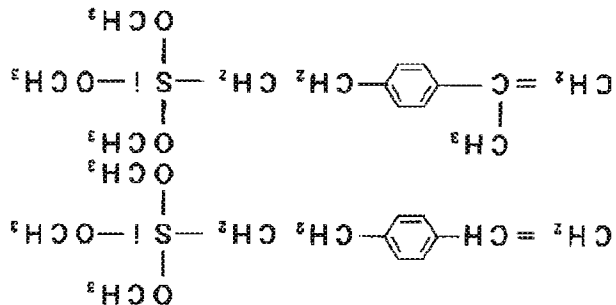
[0025]It is A among the monomers of the above-mentioned structural-formula (IV). [0026]



[Formula 16]

[0027]coming out – as a certain thing – for example [0028]

[Formula 17]



[0029]**** is mentioned.

[0030]As a monomer of the above-mentioned structural-formula (V), vinyltrimethoxysilane, vinyltriethoxysilane, etc. are mentioned, for example.

[0031]alpha which has one sort of functional groups chosen from a group of a carboxyl group, a sulfonic group, and an amino group in this invention, and beta- ethylenic unsaturated monomer (c), As a monomer which raises water solubility or water dispersibility of a copolymer, and has a carboxyl group, For example (meta), acrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, 2-carboxyl ethyl (meta) acrylate, 2-carboxyl propyl (meta) acrylate, an unsaturated monomer which has 5-carboxyl pentyl (meta-) acrylate and a hydroxyl group, and anhydrous 2 organic-functions carboxylic acid (for example, a maleic anhydride.) An equimolar addition with itaconic acid anhydride, a succinic anhydride, phthalic anhydride, etc., etc. are mentioned, and 2-(meta) acryloxyethyl sulfonic acid etc. are mentioned as a monomer which has a sulfonic group, for example. As a monomer which has an amino group, they are dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, and t , for example, - Butylamino ethyl (meta) acrylate etc. are mentioned.

[0032]In this invention, as other copolymerizable alpha and a beta- ethylenic unsaturated monomer (d), For example, methyl acrylate (meta), ethyl acrylate (meta), acrylic acid (meta) n -propyl, (Meta) Acrylic acid isopropyl, acrylic acid (meta) n -butyl, (Meta) Acrylic acid i -butyl, acrylic acid (meta) t -butyl, acrylic acid (meta) hexyl, (Meta) 2-ethylhexyl acrylate, acrylic acid (meta) n -octyl, (Meta) Decyl acrylate, acrylic acid (meta) lauryl, acrylic acid

(meta) stearyl, (Meta) Acrylic acid cyclohexyl, acrylic acid (meta) isobomyl, (Meta) Acrylic acid methoxy ethyl, acrylic acid (meta) ethoxyethyl, (Meta) Acrylic acid methoxy butyl, acrylic acid (meta) ethoxybutyl, (Meta) Acrylic acid 2-hydroxyethyl, 2-hydroxypropyl acrylate (meta), (Meta) Ester of polyether polyol, such as acrylic acid 3-hydroxypropyl, acrylic acid (meta) 4-hydroxybutyl, a polyethylene glycol, and a polypropylene glycol, and acrylic acid (meta), Which (meta) acrylic ester, Ethyl vinyl ether, n-propylvinyl ether, isopropylvinyl ether, n-butylvinyl ether, t-butylvinyl ether, Hexylvinyl ether, octylvinyl ether, cyclohexylvinyl ether, Vinyl ether, such as phenylvinyl ether, Vinyl acetate, vinyl propionate, Vinyl ester, such as lactic acid vinyl, butanoic acid vinyl, and caproic acid vinyl; Propenyl ester, such as isopropenyl acetate, (Meta) Acrylonitrile, styrene, alpha - Methylstyrene, vinyltoluene, alpha - KURORU styrene etc. are mentioned, and [for the purpose of one sort or two sorts or more], these can be chosen suitably and can be used.

[0033] A copolymerization ratio of the above-mentioned monomers preferably a monomer (a) three to 70% of the weight 5 to 40 % of the weight, it is [monomer / (b)] 20 to 70 % of the weight zero to 95% of the weight one to 25% of the weight in a monomer (c) three to 20% of the weight preferably one to 40% of the weight about 5 to 15 % of the weight, and a monomer (d). Since aqueous-izing of a copolymer or moisture powder-ization will become difficult if water repellence sufficient in less than 3 % of the weight is not acquired but a monomer (a) exceeds 70 % of the weight conversely, it is not desirable. Since it will arise and become easy to gel hydrolysis and a self-condensation reaction of alkoxysilyl groups to a polymerization process of a copolymer, or an aqueous-izing and moisture powder chemically-modified degree if a monomer (b) becomes poor [water solubility or water dispersibility of copolymer aqueous (moisture powder) liquid] in less than 1 % of the weight and exceeds 40 % of the weight conversely, it is not desirable. Since sufficient water repellence will not be acquired but a water resisting property will also fall remarkably further if aqueous-izing of a copolymer or moisture powder-ization becomes difficult and a monomer (c) exceeds 25 % of the weight conversely in less than 1 % of the weight, it is not desirable.

[0034] Copolymer solution or a water dispersion of this invention can be manufactured using a mixture of above-mentioned monomer (a) - (d) by methods, such as an emulsion polymerization method which use a neutralizer and uses aqueous-izing or a method of forming into moisture powder, and ** surface-active agent after ** solution polymerization. From a water-repellent and waterproof point of a coat obtained [especially] by this invention. ** Add water and a neutralizer to this and provide it with a manufacturing method of aqueous-izing, copolymer solution which carries out moisture powder, or a water dispersion, after performing a method, i.e., an above-mentioned monomeric mixture, in an organic solvent, performing a radical polymerization under polymerization initiator existence and obtaining a copolymer (A) solution.

[0035] Copolymer solution or a water dispersion of this invention can be manufactured without using a surface-active agent for water repellence or a water resisting property for an adverse effect according to the manufacturing method of this invention.

[0036] In this invention method, as an organic solvent used at the time of a radical polymerization, it is desirable to be able to use an alcohol system, a cellosolve system, a carbitol system, a cellosolve acetate system, etc., and to contain alcohol of the carbon numbers 1-8 30% of the weight or more especially preferably 10% of the weight or more in an organic solvent. As a radical polymerization initiator, for example 2,2-azobisisobutyronitrile, An initiator of peroxide systems, such as azo polymerization initiators, such as 2,2-azobis (2,4-dimethylvaleronitrile), or lauryl peroxide, t-butyl par 2-ethyl hexanate, and benzoyl peroxide, can be used. This radical polymerization start agent concentration has 0.3 to 10 preferred weight section to monomer 100 weight section.

[0037] In this invention method, as a neutralizer used on the occasion of aqueous-izing or moisture powder, When a monomer (c) has a carboxyl group and a sulfonic group, For example, monomethylamine, dimethylamine, trimethylamine, monoethyl amine, Diethylamine, triethylamine, monoisopropylamine, diisopropylamine, Triisopropyl amine, monobutyl amine, dibutyl amine, tributylamine, Monoethanolamine, diethanolamine,

triethanolamine, Amine, such as dimethylamino ethanol and diethylamino ethanol, When ammonia, sodium hydroxide, a potassium hydrate, etc. can be used and a monomer (c) has an amino group, organic acid, such as inorganic acid, such as chloride, sulfonic acid, and phosphoric acid, formic acid, acetic acid, propionic acid, trimethylacetic acid, acrylic acid (meta), lactic acid, can be used, for example.

[0038] A copolymer (A) obtained by the above-mentioned radical polymerization Aqueous-izing or when moisture powder is carried out. For example, after neutralizing by adding a neutralizer, agitating a copolymer (A) solution, it is also possible to carry out phase conversion of the copolymer (A) which added water or was neutralized by

adding gradually under water, but, in this case, since hydrolysis and a condensation reaction of alkoxy silyl groups advance quickly and there is a possibility of thickening and gelling, in order to prevent it, it is desirable to perform neutralization and water addition as much as possible for a short time. Although time from neutralizer addition to phase conversion by water changes with a reaction vessel, churning conditions, and ambient temperature, specifically, generally, it is convenient to consider it as less than 10 hours preferably for less than 24 hours. It is

the method of aqueous-izing or the most desirable method of carrying out moisture powder adding water in a copolymer (A) solution, and adding a neutralizer after that, without making the above-mentioned copolymer (A) solution thicken and gel. Since a neutralizer which acts also as a hydrolysis catalyst of alkoxy silyl groups, and

promotes bridge construction is blended after moisture powder according to this method, and a silanol group may exist stably, thickening and gelling can be prevented.

[0039] In this invention method, after mixing resin (B) solution which does not contain a water-repellent group in a copolymer (A) solution and in which aqueous-izing or water decentralization is possible, water and a neutralizer are added, and into this mixture, it can water-grit, or can moisture-powder-ize, and can manufacture into it.

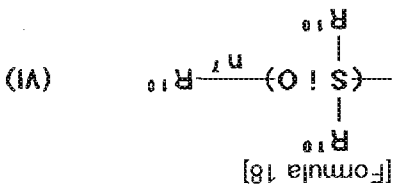
[0040] As this resin (B), if it mixes with a copolymer (A) enough, there will be no restriction in particular. For example, a copolymer obtained by carrying out copolymerization of a monomer which gives water solubility/water dispersibility, and the other monomers, and a copolymer obtained by choosing it as said monomer (c) and a

monomer (b), and (d) suitably from listings, and specifically carrying out copolymerization to them can be used. A copolymerization reaction can be performed like a copolymer (A).

[0041] As for a using rate of resin (B), when using the above-mentioned resin (B), it is preferably desirable in sum total resin solid content with a copolymer (A) to make it become 80 or less % of the weight 95 or less % of the weight. Since sufficient water repellence cannot be acquired if a using rate of this resin (B) exceeds 95 % of the weight, it is not desirable.

[0042] Furthermore, in this invention method, in order to raise water repellence in early stages of coat formation especially on the occasion of aqueous-izing of the above-mentioned copolymer (A), or formation of moisture powder, After adding a surface-active agent which has a water-repellent group in a mixed solution of a copolymer (A) solution or a copolymer (A), and resin (B), it can water-grit or water decentralize.

[0043] As this surface-active agent, what has a water-repellent group shown, for example by following structural-formula (VI) or (VII) can be used.



[0045] R¹⁰ shows a phenyl group or the alkyl group of the carbon numbers 1-6 among a formula, and n⁷ shows the integer of 5-200, respectively.

[0046]

$$[\text{Formula 19}] \quad -(\text{CF}_2)_n\text{Y} \quad (\text{VI})$$

[0047] (V) shows a hydrogen atom or a fluorine atom among a formula, and n^8 shows the integer of 1-30,

respectively.) Specifically as a surface-active agent shown by following structural-formula (VI), polyether modified silicone oil, alkyl modified silicone oil, etc. are mentioned, for example. Specifically as a surface-active agent

shown by following structural-formula (VII), perfluoroalkyl carboxylate, a perfluoro alkyl-sulfonic-acid salt, etc. are mentioned, for example. As for the addition of this surface-active agent, it is desirable that it is 5 or less % of the

weight preferably 10 or less % of the weight to resin solid content. Since the water repellence and the water resisting property of a coat which will be obtained if this addition exceeds 10 % of the weight fall, it is not

desirable.

[0048] On the other hand, by this invention, an emulsifier is used for this through a manufacturing method of the

above-mentioned **, i.e., water, distributed emulsification of the mixture of said monomer (a) - (d) is carried out, and an emulsion polymerization method performed by adding a water-soluble polymerization initiator and heating at

50-90 °C is also provided. If a redox initiator is used, it is also possible to carry out at a room temperature. As an emulsifier, for example Anionic surface active agents, such as sulfate or higher alcohol, and an alkyl-sulfonic-acid

salt, Nonionic surface active agents, such as various alkyl ether of a polyoxyethylene, alkyl ester, and alkyl allyl ether, a reactive surface active agent which has a polymerization nature unsaturation group, etc. are used. As a

polymerization initiator, hydrogen peroxide, ammonium persulfate, cumene hydroperoxide, or a water-soluble

redox initiator is used, for example.

[0049] Subsequently, in this invention, a distemper constituent which contains copolymer solution or a water

dispersion manufactured as above-mentioned as a vehicle component is provided.

[0050] Into a mixture of monomer (a) - (d) used for manufacture of the above-mentioned copolymer solution or a

water dispersion, a monomer (e) which has a carbonyl group can be further contained five to 20% of the weight

preferably one to 30% of the weight if needed from points, such as a water resisting property.

[0051] As a monomer (e) which has a carbonyl group, for example, an acrolein, diacetone acrylamide, die

acetone methacrylamide, Vinyl alkyl ketone, vinyl methyl ketone, vinyl ethyl ketone, vinyl butyl

ketone) etc. which have acetoxymethylmethacrylate, formyl styrol, and 4-7 carbon atoms are mentioned.

Among these [especially], diacetone acrylamide and die acetone methacrylamide are preferred.

[0052] The distemper constituent of this invention can contain a hydrazine derivative which has at least two -NH-

NH₂ content groups in one molecule as a cross linking agent, when the above-mentioned carbonyl group is

introduced into a copolymer. Hydrazide groups and a semicarbazide group are contained in a -NH-NH₂ content

group here.

[0053] As this hydrazine derivative, for example Oxalic acid dihydrazide, malonic acid dihydrazide, Glutaric acid

dihydrazide, amber acid dihydrazide, adipic acid dihydrazide, Saturated-fat fellows carboxylic acid dihydrazide

which has 2-18 carbon atoms, such as sebacic acid dihydrazide; Maleic acid dihydrazide; Monoolefin nature

unsaturated-dicarboxylic-acid dihydrazide, such as fumaric acid dihydrazide and itaconic acid dihydrazide;

Phthalic acid, Terephthalic acid or isophthalic acid dihydrazide, and dihydrazide of pyromellitic acid,

TORIHIDORAJUDO or tetrahydrazide; Nit RIROTORI hydrazide; Trihydrazide citrate, 1,2,4-benzene

TORIHIDORAJUDO, ethylene-diamine-tetraacetic acid tetrahydrazide, 1,4,5,8-naphthoic acid tetrahydrazide,

polyhydrazide which makes a low-grade polymer which has a carboxylic acid lower-alkyl-ester group come to

react to hydrazine or a hydrazine hydrate (hydra JINHIDO Iard) (refer to JP, 52-22878, B); Carbonic dihydrazide,

Screw semicarbazide; A polyfunctional semicarbazide produced by making a hydrazine compound and

dihydrazide of the above-mentioned illustration react to a polyisocyanate compound derived from diisocyanate,

such as hexamethylene diisocyanate and isophorone diisocyanate, and it superfluously, A drainage system polyfunctional semicarbazide produced by making dihydrazide of the above-mentioned illustration react to an isocyanate group in a reactant of this polyisocyanate compound and an active hydrogen compound containing hydrophilic radicals, such as polyether polyol and polyethylene-glycols monoalkyl ether, superfluously. Or a mixture (refer to JP, 8-151358, A and JP, 8-245878, A) of this polyfunctional semicarbazide and a drainage system polyfunctional semicarbazide, etc. are mentioned.

[0054] This hydrazine derivative is blended so that 0.01-2 mol of -NH-NH_2 groups in a hydrazine derivative may be 0.05-1.5 mol preferably to 1 mol of a carbonyl group contained in said copolymer solution or a water dispersion.

[0055] Further, if needed, additive agents for paints, such as pigments, a bulking agent, aggregate, a pigment agent, a wetting agent, a defoaming agent, a plasticizer, a film formation auxiliary agent, an organic solvent, an antiseptic, an antifungal agent, a pH adjuster, a rust-proofer, and a curing catalyst, can be chosen suitably, can be combined, and can be blended with a distemper constituent of this invention.

[0056]

[Example] Hereafter, an example is given and this invention is explained still in detail. A "weight section" and "% of the weight" are meant a "part" and "%", respectively.

[0057] Isopropyl alcohol 79 weight section was taught into the manufacture example 1 flask of a copolymer water dispersion, and temperature up was carried out, agitating to flowing-back temperature (about 84 °C).

Subsequently, the following monomeric mixture was dropped for 4 hours, maintaining temperature at flowing-back temperature.

[0058]

Styrene Ten copies 58 copies of n-butyl methacrylate Acrylic acid Seven copies KBM-502 (notes 1) 15 copies Silaplane FM-0711 (notes 2) Ten copies Azobisisobutyronitrile After riping for 2 hours, maintaining at flowing-back temperature after that [one copy], it cools to a room temperature. The almost water-white consistency copolymer solution of 55% of the nonvolatile matter was obtained. Then, the obtained copolymer solution was moved to the dilution tub, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously, carrying out temperature up to 50 °C and performing churning for 2 hours, keeping temperature at 50 °C, it cooled, and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0059] KBM-502; Shin-Etsu Chemical Co., Ltd. make, an alkoxy-silyl-groups content monomer, Silaplane (notes 2) FM-0711 : (Note 1) In the Chisso Corp. make, a poly dimethylsiloxane group content monomer, and molecular weight 1,000 example 2 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0060]

Styrene Ten copies 28 copies of n-butyl methacrylate Acrylic acid Seven copies Vinyltrimetoxysilane 15-copy Silaplane FM-0711 40 copies Azobisisobutyronitrile In one-copy example 3 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0061]

Styrene Ten copies N-butyl methacrylate 58 copies Acrylic acid Seven copies KBM-503 (notes 3) 15 copies Silaplane FM-0725 (notes 4) Ten copies Azobisisobutyronitrile One-copy (notes 3) KBM-503 : [Shin-Etsu Chemical Co., Ltd. make,] An alkoxy-silyl-groups content monomer, Silaplane (notes 4) FM-0725 : In the Chisso Corp. make, a poly dimethylsiloxane group content monomer, and molecular weight 10,000 example 4 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0062] Styrene Ten copies N-butyl methacrylate 62 copies Acrylic acid Seven copies KBM-502 Ten copies FAMAC (notes 5) Ten copies Azobisisobutyronitrile One-copy (notes 5) FAMAC : [Nippon Mektron, Ltd. make,] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as perfluoroalkyl methacrylate and 60.7 % of the weight of fluorine concentration example 5 Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained. Then, the obtained resin solution was moved to the dilution tub, the "KF-355" (Shin-Etsu Chemical Co., Ltd. make, silicone series surface-active agent) 0.4 copy was added, and it agitated for 10 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 **, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously after that and carrying out temperature up to 50 **, and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0063] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as example 6 Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained. Then, the obtained resin solution was moved to the dilution tub, the "Fluorad FC-93" (Sumitomo 3M make, fluorochemical surfactant) 0.15 copy was added, and it agitated for 10 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 **, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously after that and carrying out temperature up to 50 **, and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0064] Isopropyl alcohol 79 weight section was taught into the example 7 flask, and temperature up was carried out, agitating to flowing-back temperature (about 84 **). Subsequently, the following monomeric mixture was dropped for 4 hours, maintaining temperature at flowing-back temperature.

[0065] Styrene Ten copies 30 copies of n-butyl methacrylate Methyl methacrylate Ten copies Acrylic acid Five copies KBM-502 Ten copies Silaplane FM-071 1 35 copies Azobisisobutyronitrile After riping for 2 hours, maintaining at flowing-back temperature after that [one copy], to a room temperature. It cooled and the almost water-white consistency copolymer solution (A) of 56% of the nonvolatile matter was obtained. In another flask, except having used the following mixture as a dropped monomeric mixture, the polymerization reaction was performed like the copolymer solution (A), and the almost water-white consistency copolymer solution (B) of 56% of the nonvolatile matter was obtained.

[0066] Styrene Five copies N-butyl methacrylate 26-copy methyl methacrylate 37 copies Acrylic acid 2-hydroxyethyl Seven copies Acrylic acid Ten copies KBM-502 15 copies Azobisisobutyronitrile 18 copies of copolymer solutions (A) obtained by the one-copy above like, And after teaching 162 copies of copolymer solutions (B) to a dilution tub, respectively and agitating them for 15 minutes, it cooled, after performing churning for 2 hours, keeping temperature at 50 ** after 816.5 copies of deionized water having added 13.3 copies of triethylamines continuously and carrying out temperature up to 50 **, and the water dispersion of the opalescence of 10% of a nonvolatile matter was obtained.

[0067] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as example 8 Example 1, and the almost water-white consistency copolymer solution (C) of 56% of the nonvolatile matter was obtained.

[0068] In another flask, except having used the following mixture as a dropped monomeric mixture, the polymerization reaction was performed like the copolymer solution (C), and the almost water-white consistency copolymer solution (D) of 56% of the nonvolatile matter was obtained.

[0069] N-butyl methacrylate 22 copies Methyl methacrylate 48 copies Acrylic acid 30 copies Azobisisobutyronitrile 108

copies of copolymer solutions (C) obtained by the one-copy above like, And after teaching 72 copies of copolymer solutions (D) to a dilution tub, respectively and agitating them for 15 minutes, it cooled, after performing churning for 2 hours, keeping temperature at 50 ° after 807.1 copies of deionized water having added 22.7 copies of triethylamines continuously and carrying out temperature up to 50 °, and the almost water-white water dispersion of 10% of the nonvolatile matter was obtained.

[0070] 0.15 copy of dodecylbenzenesulfonic acid ammonium and 95 copies of deionized water were taught into the example 9 flask, and temperature up was carried out to 85 °. Then, after using the homomixer for 80 copies of water and distributing the following monomeric mixture, 1.0 copy of ammonium persulfate was added. The water dispersion was dropped into the flask over 5 hours, it was made to ripe for further 2 hours, and the emulsion of the opalescence of 39% of a nonvolatile matter was obtained. The obtained emulsion was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0071]

n-butyl methacrylate 25.5 copies Acrylic acid n-butyl . Copies [50.5] Acrylic Acid 2-Hydroxyethyl 3 Part Acrylic Acid 1 Part Silaplane FM-0711 10 Part KBM-503 10 Part Dodecylbenzenesulfonic Acid Ammonium in 8.7-Copy Comparative Example 1, Although it carried out like Example 1 except having used the following monomeric mixture as a dropped monomeric mixture and the water dispersion was tried with the method of profitably, generation of a coarse particle and sedimentation took place and the good state was not obtained.

[0072]

Styrene Ten copies 73 copies of n-butyl methacrylate Acrylic acid Seven copies Silaplane FM-0725 Ten copies Azobisisobutyronitrile in one-copy comparative example 2 Example 1, Although it carried out like Example 1 except having used the following monomeric mixture as a dropped monomeric mixture and the water dispersion was tried with the method of profitably, generation of a coarse particle and sedimentation took place and the water dispersion of the good state was not obtained.

[0073]

Styrene Ten copies 73 copies of n-butyl methacrylate Acrylic acid Seven copies Ten copies of FAMAC(s) Azobisisobutyronitrile in one-copy comparative example 3 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, the polymerization reaction was performed in the flask by the same operation as Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained.

[0074]

N-butyl methacrylate 22 copies Methyl methacrylate 38 copies Acrylic acid 30 copies Silaplane FM-0711 Ten copies Azobisisobutyronitrile The resin solution obtained continuously one copy is moved to a dilution tub, it cooled, after performing churning for 2 hours, keeping temperature at 50 ° after adding 787.8 copies of deionized water, and 42 copies of triethylamines and carrying out temperature up to 50 °, and the almost water-white solution of 10% of the nonvolatile matter was obtained.

[0075] in comparative example 4 Example 1, except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion with almost translucent colorlessness of 10% of the nonvolatile matter was obtained.

[0076]

Styrene Ten copies N-butyl methacrylate 48 copies Methyl methacrylate 20 copies Acrylic acid Seven copies KBM-502 15 copies Azobisisobutyronitrile Ethylene-glycol-monobutyl-ether 70 weight section is taught into one-copy comparative example 5 flask, Temperature up was carried out agitating to 95 °. Subsequently, the following monomeric mixture was dropped for 4 hours, keeping temperature at 95 °.

[0077]

[0079] n-butyl methacrylate 25.5 copies Acrylic acid n-butyl . Copies [50.5] Acrylic Acid 2-Hydroxyethyl. 3 Part Acrylic Acid 1 Part Silaplane FM-0711 20 Part Dodecylbenzenesulfonic Acid Ammonium Water Dispersion or Solution of Examples 1-9 and Comparative Examples 3-6 Obtained as 8.7-Copy System-Performance-Testing above, All show good water dispersibility.

These were painted by a 50-micrometer applicator to the glass plate, respectively, and after making it dry at 100 °C for 2 hours, the following system performance testing was presented.

比較例	実施例	
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Table 1

[0084] In creation example 10 Example 1 of distemper, except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0085]

Styrene Ten copies 48 copies of n-butyl methacrylate Diacetone acrylamide Ten copies Acrylic acid Seven copies KBM-502 15 copies Siliplane FM-0711 Ten copies Azobisisobutyronitrile To the water dispersion obtained one

copy. 5.2 copies of adipic acid dihydrazide was added, it mixed, and the clear coating material was obtained. After painting this by a 50-micrometer applicator to the glass plate and making it dry at 100 °C for 2 hours, when the same system performance testing as the above was presented, paint film appearance and the water resisting property of all were O, and the water contact angle was 93 degrees.

[0086]

[Function and Effect(s) of the invention] In the copolymer solution or the water dispersion of this invention. The alkoxysilyl groups introduced into the copolymer by using a monomer (b) as a copolymerization ingredient hydrolyzes under existence of water, and turns into a silanol group, it can conquer, in order that this silanol group may raise water solubility or water dispersibility remarkably, and it can become possible to lessen the amount of copolymerization of the monomer (c) which has a functional group which moreover gives water solubility/water dispersibility, and water repellence can be raised. In the drying process of the coat by this copolymer solution or a water dispersion, in order to form the firm structure of cross linkage by the self-condensation reaction of silanol groups, the coat which shows a good water resisting property is obtained.

[0087] Therefore, the distemper constituent using the copolymer solution or the water dispersion of this invention as a vehicle component can form the coat excellent in water repellence and a water resisting property.

[Translation done.]

AQUEOUS SOLUTION OR AQUEOUS DISPERSION OF COPOLYMER HAVING
WATER-REPELLING PROPERTY, ITS PRODUCTION AND AQUEOUS COATING
COMPOSITION CONTAINING THE SAME

Publication number JP11124419

Publication date: 1999-05-11

Inventor: MIYATA NAOKI, NUMA NOBUSHIGE

Applicant: KANSAI PAINT CO. LTD.

Classification:

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C09D155/00; C08K5/00; C08F220/00; C08F290/00; C08L33/00; C09D4/06;
C09D133/06; C09D155/00; C08F220/10; C08F290/06; C08L33/06; C09D4/06;
C09D133/06; C08F220/06; C08F220/10; C08F220/06; C08F220/22;
C08F220/42; C08F230/08

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Application number: JP19970290018 19971022

Priority number(s): JP19970290018 19971022

View INPADOC patent family

Abstract of JP11124419

PROBLEM TO BE SOLVED: To obtain the subject aqueous solution useful as a coating resin capable of forming a coating film having excellent water-repellence and water resistance by copolymerizing a mixture containing a monomer having a specific structure, a monomer having an alkoxyethyl group, an ethylenic unsaturated monomer, etc. SOLUTION: The objective aqueous solution is produced by copolymerizing a monomer mixture containing (A) 3-70 wt.% of one or more monomers selected from the monomer of the formula I (R<1> is H or methyl; R<2> is phenyl or a 1-6C alkyl; n<1> is 1-10; n<2> is 5-200) and the formula II (R<3> is H or methyl; X is H or F; n<3> is 1-8; n<4> is 1-30), (B) 1-40 wt.% of a monomer having an alkoxyethyl group, (C) 1-25 wt.% of an alpha, β-ethylenic unsaturated monomer having a functional group selected from carboxyl group, sulfonic acid group and amino group and (D) 0-95 wt.% of other alpha, β-ethylenic unsaturated monomers.

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(54) 【発明の名称】 撥水性を有する共重合体水溶液もしくは水分散液、及びその製造方法、及びこれを含む水性塗料組成物

(57) 【要約】

【課題】 撥水性及び耐水性に優れた塗膜を形成し得る塗料用樹脂として有用な共重合体水溶液もしくは水分散液、及びその製造方法、及びこれを含む水性塗料組成物を提供する。

【解決手段】 (a) 2種の撥水性を付与する単量体から選ばれた少なくとも1種の単量体を3〜70重量%、(b) アルコキシシリル基を有する単量体を1〜40重量%、(c) カルボキシ基、スルホン酸基及びアミノ基の群から選ばれた1種の官能基を有する α 、 β -エチレン性不飽和単量体を1〜25重量%、および(d) その他の共重合可能な α 、 β -エチレン性不飽和単量体を0〜95重量%含有する単量体混合物を共重合する。

3~70%喜喜%

[74]



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4

下



55



*

2

4

2

7

23

4

1

1

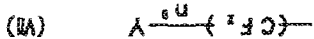
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五

五

1



(式中、Yは水素原子又はフッ素原子を、 n^6 は1〜30の整数を夫々示す。)

【請求項8】 請求項1記載の共重合体水溶液もしくは水分散液を乳比重合法を用いて得る共重合体水溶液とし

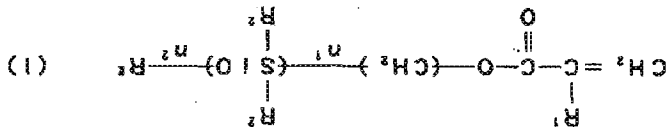
＜は水分散液の製造方法。

【請求項9】 (a) 下記の構造式(1)及び(11)で

示される単量体から選ばれた少なくとも1種の単量体を

3〜70重量%、

【化7】



【従来技術及びその課題】ポリシメチルシリロキサンに代

表されるような低分子量の撥水性剤を塗料に混合すること

により乾燥塗膜に撥水性を付与する方法は従来からよく

知られているが、経時で撥水性が低下するなどの問題点

があった。これに対してシリコン変性アクリル樹脂の

ように樹脂中に撥水性基を導入する方法をとることによ

って撥水持続性の高い撥水性塗膜を得ることが可能であ

る。

【0003】大気汚染防止および塗装時の衛生の面か

ら、また防災上からもこのような撥水性樹脂の水性化が

強く求められているが、従来の撥水性樹脂は一般に疎水

性が強く、水溶化、水分散が難しい。このような問題点

を解決する手段として、例えば特開平2-150475

号公報では、オルガノシリロキサンフクロモノマーと

α 、 β -エチレン性不飽和単量体を乳比重合法で混合すること

による水性化の方法が開示されている。しかしながらこ

の方法では、親水性の高い界面活性剤を使用せざるを得

ず、十分な撥水性を示すまでには到らなかった。またカ

ルボキシシル基等の親水性官能基導入により撥水性樹脂を

自己乳化させる方法もあるが、極端に高い樹脂酸価が必

要となり、耐水性の面から好ましい方法とは言えなかつ

た。

【0004】

【課題を解決するための手段】本発明者は、上記問題

を解決すべく鋭意検討した結果、撥水性を付与する単量

体及びアルコキシシリル基を有する単量体を必須とする

ことにより、塗膜に優れた撥水性及び耐水性を付与しう

る水性樹脂が得られることを見出し本発明に到達した。

【0005】即ち本発明は、(a)下記の構造式(1)

及び(11)で示される単量体から選ばれた少なくとも1

種の単量体を3〜70重量%、

【0006】

【化9】

【化6】

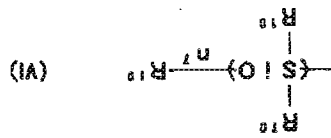
体水溶液もしくは水分散液の製造方法。

れる撥水性基を有するものである請求項5記載の共重合

【請求項7】 界面活性剤が、下記構造式(VII)で示さ

基を、 n^7 は5〜200の整数を夫々示す。)

(式中、 R^{10} はフェニル基又は炭素数1〜6のアルキル



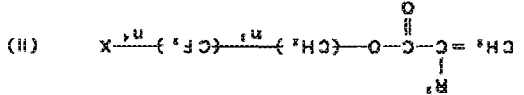
(式中、 R^1 は水素原子又はメチル基を、 R^2 は同一又

は異なつてフェニル基又は炭素数1〜6のアルキル基

を、 n^1 は1〜10の整数を、 n^2 は5〜200の整数

を夫々示す。)

【化8】



(式中、 R^2 は水素原子又はメチル基を、Xは水素原子

又はフッ素原子を、 n^3 は1〜8の整数を、 n^4 は1〜

30の整数を夫々示す。)

(b) アルコキシシリル基を有する単量体を1〜40重

量%、(c) カルボキシシル基、アルボノ酸基及びアミノ

基の群から選ばれた1種の官能基を有する α 、 β -エチ

レン性不飽和単量体を1〜25重量%、および(d) そ

の他の共重合可能な α 、 β -エチレン性不飽和単量体を

0〜95重量%含有する単量体混合物を共重合してなる

撥水性を有する共重合体水溶液もしくは水分散液をビ

クル成分として含有してなる水性塗料組成物。

【請求項10】 単量体混合物が、(e) カルボニル基

を有する単量体を1〜30重量%含有する請求項9記載

の水性塗料組成物。

【請求項11】 架橋剤として、1分子中に少なくとも

2個の-NH-NH₂含有基を有するヒラジン誘導体

を含有する請求項10記載の水性塗料組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、撥水性を有する共

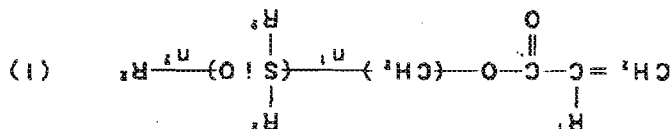
重合体水溶液もしくは水分散液に関する。詳しくは撥水性

及び耐水性に優れた塗膜を形成し得る塗料用樹脂として

有用な共重合体水溶液もしくは水分散液及びその製造方

法、及びこれを含む水性塗料組成物に関する。

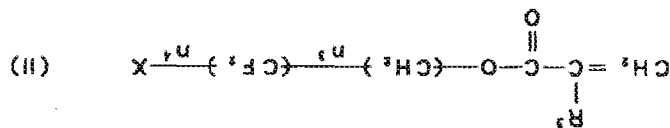
【0002】



00の整数を夫々示す。)

【0008】

【化10】

【0007】(式中、R¹は水素原子又はメチル基を、R²は同一又は異なるフエニル基又は炭素数1～6のアルキル基を、n¹は1～10の整数を、n²は5～2【0009】(式中、R²は水素原子又はメチル基を、Xは水素原子又はフッ素原子を、n³は1～8の整数を、n⁴は1～30の整数を夫々示す。)

(b)アルコキシシリル基を有する単量体を1～40重

量%、(c)カルボキシシリル基、アルホキシシリル基及びアミノ

基の群から選ばれる1種の官能基を有するα、β-エチ

レン性不飽和単量体を1～25重量%、および(d)そ

の他の共重合可能なα、β-エチレン性不飽和単量体を

0～95重量%含有する単量体混合物を共重合すること

を特徴とする親水性を有する共重合体水溶液もしくは水

分散液、及びその製造方法、及び該共重合体水溶液とし

ては水分分散液をビニル成分として含有する水性塗料組

成物を提供するものである。

【0010】

【発明の実施の形態】本発明において上記の構造式

(1)及び(11)で示される単量体から選ばれる少なく

とも1種の単量体(a)は、共重合体に親水性を付与す

るものであり、上記構造式(1)で示されるポリシロキ

サン鎖を有する単量体(a-1)及び上記構造式(11)

で示されるフッ素含有する単量体(a-2)のいずれ

か1方又は両方を使用できる。

【0011】上記構造式(1)で示される単量体(a-

1)において、R¹は水素原子又はメチル基であり、R²はフエニル基又は炭素数1～6のアルキル基であるが、必ずしも互いに同じものである必要はない、n¹は1～100の整数、n²は5～200、好ましくは15～150の整数である、n²が5未満では十分な親水性

が得られず、逆に200を超える場合は共重合体の親水

性が不足し、水溶性もしくは水分散性不良となるので望

ましくない、該単量体(a-1)の具体例として、市販

品では、「サイラフレンFM-0711」、「サイラ

フレンFM-0721」、「サイラフレンFM-0

725」(いずれもチソ社製)等が挙げられる。

【0012】上記構造式(11)で示される単量体(a-

2)において、R³は水素原子又はメチル基であり、Xは水素原子またはフッ素原子である、n³は1～8の整数、n⁴は1～30の整数である、n⁴が30を超え

ると、他の単量体との混合性や共重合性が劣り、また親

水性が不足するため水溶性もしくは水分散性不良となる

ので望ましくない、該単量体(a-2)の具体例とし

て、例えば2, 2, 2-トリフルオロエチル(メタ)フ

クリレート、2, 2, 3, 3-テトラフルオロプロピル

(メタ)フクリレート、2-(メソチカフルオロオク

サル)エチル(メタ)フクリレート、2-(ノナチカフ

ルオロシフル)エチル(メタ)フクリレートなど、市販

品では「FAMAC」(日本マクトロ社製)、「ビス

コート8FM」、「ビスコート17FM」(いずれも大

阪有機化学工業社製)などが挙げられる。

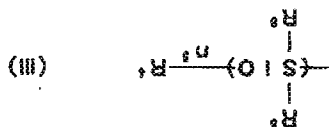
【0013】本発明においてアルコキシシリル基を有す

る単量体(b)は、下記構造式(111)で示されるアル

コキシシリル基を有するものであり、

【0014】

【化11】

【0015】(式中、R¹は炭素数1～10のアルキル基を、R²及びR³は同一又は異なるフエニル基、炭素

数1～6のアルキル基又は炭素数1～10のアルコキシ

ル基を、n⁵は1～4の整数を夫々示す。また、n⁵が2以上するとき、R⁵同志及びR⁶同志は同じであつて

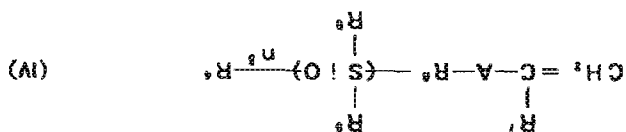
も異なつていてもよい。)

その代表例としては下記構造式(1V)及び(1V)で示さ

れる単量体を挙げることができる。

【0016】

【化12】



【0019】を示す。R¹は水素原子又はメチル基を、

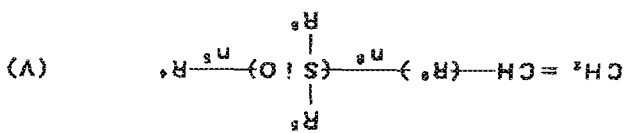
R²は炭素数1～6の2面の脂肪族飽和炭化水素基を夫

々示す。R³、R⁴及びR⁵は、夫々前記と同じ

意味を有する。）

【0020】

【化14】



【0025】また上記構造式(IV)の単量体のうちAがメチルジエトキシシランなどが好適に例示できる。

【0026】

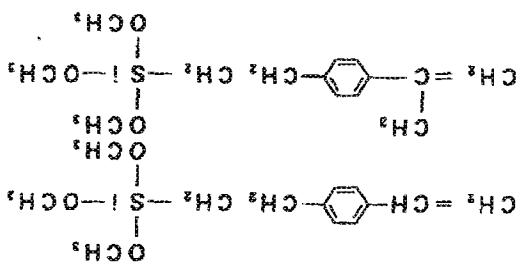
【化16】



【0027】であるものとしては、例えば

【0028】

【化17】



【0029】などが挙げられる。

【0030】上記構造式(V)の単量体としては、たと

えばビニルトリメトキシシラン、ビニルトリエトキシシ

ランなどが挙げられる。

【0031】本発明においてカルボキシ基、アルホソ

酸基及びアミノ基の群から選ばれた1種の官能基を有す

るα、β-エチレン性不飽和単量体(c)は、共重合体

の水溶性もしくは水分散性を向上させるものであり、カ

ルボキシ基を有する単量体としては、例えば(メタ)

アクリル酸、クロト酸、イタコン酸、マレイン酸、フ

マル酸、2-カルボキシエチル(メタ)アクリレ-

ート、2-カルボキシプロピル(メタ)アクリレート、

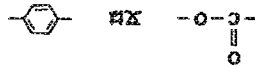
5-カルボキシペンチル(メタ)アクリレート、水酸

基を有する不飽和単量体と無水2官能カルボン酸(例え

【0017】(式中、Aは、

【0018】

【化13】



【0021】(式中、R⁹は炭素数1～6の2面の脂肪

族飽和炭化水素基を、R⁵は0又は1を示す。R⁴、R

【0022】(IV)及び(V)において、R³及びR⁹に

よって示される炭素数1～6の2面の脂肪族飽和炭化水

素基としては、直鎖又は分枝状のアルキル基、例え

ばメチル、エチル、プロピル、1,2-、1,3-

ブチル、3-ブチル、ペンチル、ヘキシル、ヘ

キシル、ヘキシル、ヘキサメチル基などを挙げられ

る。R⁵及びR⁹で示される炭素数1～6のアルキル基

としては、直鎖又は分枝状のアルキル基、例え

ばメチル、エチル、プロピル、1,2-、1,3-

ブチル、3-ブチル、ペンチル、ヘキシル、ヘ

キシル、ヘキシル、ヘキサメチル、イソヘキシル

、1-メチルペンチルなどを挙げられる。R⁴で示さ

れる炭素数1～6のアルキル基としては、R⁵及びR

【0023】で示される炭素数1～6のアルキル基として例示した

ものの他に、さらにn-ヘプチル、2-エチルヘキシル

、n-オクチル、n-ニル、n-デシルなどを挙げ

られる。R⁵及びR⁹で示される炭素数1～10のアル

コキシ基としては、直鎖又は分枝状のアルコキシ

基、例えメトキシ、エトキシ、n-プロポキシ、イソ

プロポキシ、n-、i-、sec-又はtert-ブ

キ、n-ペンチオキシ、イソペンチオキシ、n-ヘキシル

オキシ、イソヘキシルオキシ、n-オクチルオキシなど

【0022】上記構造式(IV)の単量体のうちAが

【0023】

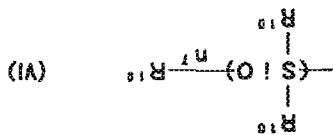
【化15】



【0024】であるものとしては、例えはA-(メタ)

アクリロイルオキシエトキシシラン、γ-(メタ)ア

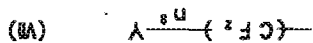
リロイルオキシプロピルトリメトキシシラン、γ-(メ



【0045】(式中、 R^{10} はフェニル基又は炭素数1〜6のアルキル基を、 n^7 は5〜200の整数を夫々示す。)

【0046】

【化19】



【0047】(式中、 Y は水素原子又はフッ素原子を、 n^8 は1〜30の整数を夫々示す。)

【0048】一方本発明では、前記の製造方法、即ち水を媒体として、これに乳化剤を用いて前記単量体

(a)〜(d)の混合物を分散乳化させ、水溶性の重合開始剤を加えて50〜90℃で加熱することによって行われる乳化重合法をも提供するものである。レゾルノス開始剤を用いると室温で行なうことも可能である。乳化剤としては、例えば高級アルコールの硫酸塩、アルキルアルコールの各種アルキルエーテル、アルキルエーテル、アルキルアルリルエーテルなどの非イオン界面活性剤、及び重合性不飽和基を有する反応性界面活性剤などが使用される。重合開始剤としては、例えば過酸化水素、過硫酸アモモニウム、クメンヒドロパーオキシド、あるいは水溶性レゾルノス開始剤などが用いられる。

【0049】次いで本発明では、上記の通り製造される共重合体水溶液もしくは水分散液をビニル成分として含む水性塗料組成物を提供するものである。

【0050】上記共重合体水溶液もしくは水分散液の製造に用いられる単量体(a)〜(d)の混合物には、さらに耐水性などの点からカルボニル基を有する単量体

(e)を、必要に応じて1〜30重量%、好ましくは5〜20重量%含有することができる。

【0051】カルボニル基を有する単量体(e)としては、例えばアクリロイン、ダイアセトペンタクリルアミド、ダイアセトペンタクリルアミド、アセトアセトキシエチルメタクリレート、ホルミルアセトロール、4〜7個

【0038】上記ラジカル重合によって得られた共重合

体(A)を水溶性もしくは水分散する場合、例えば共重合体(A)を水溶液を攪拌しながら中和剤を添加して中和を行なった後、水を添加するか、中和した共重合体(A)を水中に徐々に添加することによって相転換することも可能であるが、この場合アルコキシシリル基の加水分解及び縮合反応が急遽に進行し、増粘、ゲル化することおそれがあるため、それを防止するために中和及び水添加をできるだけ短時間でいうことが望ましい。具体的には、中和剤添加から水による相転換までの時間は、反応容器、攪拌条件、雰囲気温度によって異なるが、一般には24時間以内、好ましくは10時間以内とするのが好都合である。

上記共重合体(A)溶液を、増粘やゲル化させずに水溶性もしくは水分散させる最も好ましい方法は、共重合体(A)溶液に水を添加し、その後中和剤を添加する方法である。この方法によればアルコキシシリル基の加水分解触媒としても作用し架橋を促進する中和剤が水分散後に配合されるので、シラノール基が安定に存在しうることから増粘、ゲル化を防止できる。

【0039】また本発明方法においては、共重合体(A)溶液に、親水性基を含まない水溶性もしくは水分散可能な樹脂(B)溶液を混合してから、該混合物に水および中和剤を添加して水溶性もしくは水分散化して製造することができる。

【0040】該樹脂(B)としては、共重合体(A)と十分混合するものであれば特に制限はなく、例えば水溶性/水分散性を付与する単量体及びその他の単量体を共重合することにより得られる共重合体、具体的には前記単量体(c)及び単量体(b)、(d)に列記の中から適宜選択して共重合することにより得られる共重合体を

使用することができる。共重合反応は共重合体(A)と同様に進行することができる。

【0041】上記樹脂(B)を用いる場合、樹脂(B)の使用割合は、共重合体(A)との合計樹脂固形分中に95重量%以下、好ましくは80重量%以下となるようにするが望ましい。該樹脂(B)の使用割合が95重量%を超えると十分な親水性を得られない場合があるの

【0042】さらに本発明方法において、上記共重合体(A)の水溶性もしくは水分散化に際して特に塗膜形成初期の親水性を向上させる目的で、共重合体(A)溶液もしくは共重合体(A)及び樹脂(B)の混合溶液に親水性基を有する界面活性剤を添加してから水溶性もしくは水分散化することができる。

【0043】該界面活性剤としては、例えば下記構造式(VI)または(VII)で示される親水性基を有するものが使用できる。

【化18】

【0044】

【化18】

【0052】本発明の水性塗料組成物は、上記カルボニル基が共重合体に導入された場合には、架橋剤として、1分子中に少なくとも2個の $-NH-NH_2$ 含有基を有するとクローズド環体を含むことができる。ここで $-NH-NH_2$ 含有基には、ヒドロキシ基、セミカルバ

子を有する飽和脂肪族カルボン酸ジエトラジエ、アレイノ酸ジエトラジエ、アラル酸ジエトラジエ、アタクメ酸ジエトラジエ等のモノオレフィン性不飽和カルボン酸ジエトラジエ、アラル酸、アレノタル酸またはイソノタル酸ジエトラジエ、ならびにヒロキソット酸のジエトラジエ、アリエトラジエまたはアトラジエ、ニマリ

(「ヒラジエヒラード」)と風乾させるポリヒメラジク(特公昭52-22878号参照)、焼炭ジヒメラジク、ヒメスミカルビナ、ヘキサチレニジヒメラードやイソホロジヒメラード等のジヒメラードネート及びそれより誘導されるポリイソシアネート化合物

1166-0 1166X

KBM-502 (注1)

44571-7FM-07

ら2時間熟成した後室温まで

【0059】(注1) KBM-502: 信越化学工業社
製、アルコキシシリル基含有単量体、

1152-0 雜 11166x

1997-1998

【0055】本発明の水性塗料組成物には、さらに必要に応じて、顔料、充實剤、骨材、顔料分散剤、流延剤、消泡剤、可塑剤、造膜助剤、有機溶剤、防腐剤、防かび剤、pH調整剤、防錆剤、硬化触媒などの適宜添加剤を適宜選択し組合わせて配合することができる。

【0056】

フラスコ中にイソプロピルアルコール79重量部を仕込み、蒸気温度（約84℃）まで撹拌を行いながら昇温した。次いで温度を蒸気温度に保ちながら下記重量比混合物を4時間滴下した。

【0058】

585

158

04

— FM —

288

15 数

【0061】
 い、不揮発分10%のうすい乳白色の水分散液を得た。
 40部
 1部

【注4】
 10部
 58部
 7部
 15部
 10部
 1部

実施例4
 実施例1において、滴下する単量体混合物として下記の
 単量体混合物を用いた以外は実施例1と同様にして行
 い、不揮発分10%のうすい乳白色の水分散液を得た。
 【0062】

10部
 62部
 7部
 10部
 10部
 10部
 1部

ラスコ中で重合反応を行い、不揮発分56%のほぼ無色
 透明の粘潤な共重合体溶液を得た。続いて得られた樹脂
 溶液を希釈槽に移し、「フロラーF93」（住友
 スリーエム社製、フッ素系界面活性剤）0.15部を添
 加して10分間攪拌した。その後脱イオン水820部、
 続いてトリエチルアミン9.8部を加えて50℃に昇温
 したのち温度を50℃に保ちながら2時間攪拌を行っ
 てから冷却し、不揮発分10%のほぼ無色の半透明な水分
 散液を得た。
 【0064】実施例7

フラスコ中にイソプロピルアルコール79重量部を仕込
 み、還流温度（約84℃）まで攪拌を行いながら昇温し
 た。次いで温度を還流温度に保ちながら下記単量体混合
 物を4時間滴下した。
 【0065】

10部
 30部
 10部
 5部
 10部
 35部
 1部

液（A）と同様にして重合反応を行い、不揮発分56%
 のほぼ無色透明の粘潤な共重合体溶液（B）を得た。
 【0066】

5部
 26部

サイラアレーンFM-0711
 フビエスイソチロニトリル

実施例3
 実施例1において、滴下する単量体混合物として下記の
 単量体混合物を用いた以外は実施例1と同様にして行

スチレン

メタクリル酸n-ブチル

アクリル酸

KBM-503（注3）

サイラアレーンFM-0725

フビエスイソチロニトリル

（注3）KBM-503：信越化学工業社製、アルコキ

シシリル基含有単量体、

（注4）サイラアレーンFM-0725：チッソ社製、

ポリジメチルシロキサン基含有単量体、分子量10,0

00

スチレン

メタクリル酸n-ブチル

アクリル酸

KBM-502

FAMAC（注5）

フビエスイソチロニトリル

（注5）FAMAC：日本メクトロン社製、パ-フルオ

ロアルキルメタクリレート、フッ素濃度60.7重量%

実施例5

実施例1と同様の単量体混合物を用いて同様の操作でフ

ラスコ中で重合反応を行い、不揮発分56%のほぼ無色

透明の粘潤な共重合体溶液を得た。続いて得られた樹脂

溶液を希釈槽に移し、「KF-355」（信越化学工業

社製、シリコン系界面活性剤）0.4部を添加して1

0分間攪拌した。その後脱イオン水820部、続いてト

リエチルアミン9.8部を加えて50℃に昇温したのち

温度を50℃に保ちながら2時間攪拌を行ってから冷却

し、不揮発分10%のほぼ無色の半透明な水分散液を得

た。

【0063】実施例6

実施例1と同様の単量体混合物を用いて同様の操作でフ

スチレン

メタクリル酸n-ブチル

アクリル酸

KBM-502

サイラアレーンFM-0711

フビエスイソチロニトリル

その後還流温度に保ちながら2時間加熱した後室温まで

冷却し、不揮発分56%のほぼ無色透明の粘潤な共重合

体溶液（A）を得た。別フラスコにおいて、滴下する単

量体混合物として下記混合物を用いた以外は共重合体溶

スチレン

メタクリル酸n-ブチル

メタクリル酸メチル

アクリル酸2-ヒドロキシエチル

アクリル酸

KBM-502

アビエスノブチロニトリル

上記のように得られた共重合体溶液(A)18部、及び

共重合体溶液(B)162部を希釈槽に夫々仕込み、1

5分間攪拌してから、脱イオン水816、5部、続いて

トリエチルアミン13、3部を加えて50℃に昇温した

のち温度を50℃に保ちながら2時間攪拌を行ってから

冷却し、不揮発分10%の乳白色の水分散液を得た。

【0067】実施例8

実施例1と同様の単量体混合物を用いて同様の操作でフ

メタクリル酸n-ブチル

メタクリル酸メチル

アクリル酸

アビエスノブチロニトリル

上記のように得られた共重合体溶液(C)108部、及

び共重合体溶液(D)72部を希釈槽に夫々仕込み、1

5分間攪拌してから、脱イオン水807、1部、続いて

トリエチルアミン22、7部を加えて50℃に昇温した

のち温度を50℃に保ちながら2時間攪拌を行ってから

冷却し、不揮発分10%のほぼ無色透明な水分散液を得

【0070】実施例9

フラスコ中にアビエスノブチロニトリル

メタクリル酸n-ブチル

アクリル酸n-ブチル

アクリル酸2-ヒドロキシエチル

アクリル酸

サイラブレ-ンFM-0711

KBM-503

アビエスノブチロニトリル

実施例1において、滴下する単量体混合物として下記の

単量体混合物を用いた以外は実施例1と同様にして行

アクリル酸

メタクリル酸n-ブチル

アクリル酸

サイラブレ-ンFM-0725

アビエスノブチロニトリル

比較例2

実施例1において、滴下する単量体混合物として下記の

単量体混合物を用いた以外は実施例1と同様にして行

アクリル酸

メタクリル酸n-ブチル

アクリル酸

FAMAC

アビエスノブチロニトリル

比較例3

実施例1において、滴下する単量体混合物として下記の

1部

10部

7部

73部

10部

【0073】

降が起こり、良好な状態の水分散液は得られなかった。

い、水分散液を得ようと試みたが、粗大粒子の生成、沈

1部

10部

7部

73部

10部

【0072】

降が起こり、良好な状態の水分散液は得られなかった。

い、水分散液を得ようと試みたが、粗大粒子の生成、沈

8、7部

10部

10部

1部

3部

50、5部

25、5部

【0071】

オン水で不揮発分10%に希釈して性能試験に用いた。

色のエマルジョンを得た。得られたエマルジョンは脱イ

滴下し、さらに2時間熟成させて不揮発分39%の乳白

色を添加した。その水分散液を5時間かけてフラスコ中に

サーを用いて分散してから過硫酸アモニウム1、0部

した、続いて下記の単量体混合物を水80部にホモミキ

0、15部と脱イオン水95部を仕込み、85℃に昇温

1部

30部

48部

22部

【0069】

色透明の粘潤な共重合体溶液(D)を得た。

と同様にして重合反応を行い、不揮発分56%のほぼ無

物として下記混合物を用いた以外は共重合体溶液(C)

【0068】別フラスコにおいて、滴下する単量体混合

透明の粘潤な共重合体溶液(C)を得た。

フラスコ中で重合反応を行い、不揮発分56%のほぼ無色

1部

15部

10部

7部

37部

単量体混合物を用いた以外は実施例1と同様の操作でフラスコ中で重合反応を行い、不揮発分5.6%のほぼ無色

メタクリル酸n-ブチル
メタクリル酸メチル
アクリル酸
サトラブレンFM-0711
アビエスイソチロニトリル

続いて得られた樹脂溶液を希釈槽に移し、脱イオン水7.8部、トリエチルアミン4.2部を加えて50℃に昇温したのち温度を50℃に保ちながら2時間攪拌を行ってから冷却し、不揮発分1.0%のほぼ無色透明な水溶液を得た。

【0075】比較例4

アクリル

メタクリル酸n-ブチル

メタクリル酸メチル

アクリル酸

KBM-502

アビエスイソチロニトリル

比較例5

フラスコ中にエチレンジリコールモノブチルエーテル7.0重量部を仕込み、95℃まで攪拌を行いながら昇温し

メタクリル酸メチル
メタクリル酸n-ブチル

アクリル酸

アクリル酸4-ヒドロキシブチル

アビエスイソチロニトリル

その後温度を95℃に保ちながら2時間加熱した後室温

まで冷却し、中和剤としてトリエチルアミン2.1部を加

えた後、エチレンジリコールモノブチルエーテル4.5部

で希釈して不揮発分4.3%のほぼ無色透明の粘稠な樹脂

溶液を得た。得られた樹脂溶液を脱イオン水で不揮発分

1.0%に希釈して性能試験に用いた。

【0078】比較例6

フラスコ中にアビエスイソチロニトリルアミン2.1部を仕

メタクリル酸n-ブチル
メタクリル酸メチル
アクリル酸n-ブチル
アクリル酸2-ヒドロキシエチル
アクリル酸
サトラブレンFM-0711
アビエスイソチロニトリル

性能試験

上記の通り得られた実施例1～9および比較例3～6の

水分散液もしくは水溶液は、いずれも良好な水分散性を

示しており、これらをガラス板に50μmアクリルタ

ーで夫々塗装し、100℃で2時間乾燥させた後、下記

の性能試験に供した。結果を表1に示す。

【0080】(*1) 塗膜外觀：目視で評価し、良好な

ものを○、ツヤびけが認められるものを×とした。

【0081】(*2) 親水性：各塗装板上に0.03cc

透明の粘稠な共重合体溶液を得た。

【0074】

2.2部

3.8部

3.0部

1.0部

1部

実施例1において、滴下する単量体混合物として下記の単量体混合物を用いた以外は実施例1と同様にして行い、不揮発分1.0%のほぼ無色の半透明な水分散液を得た。

【0076】

10部

4.8部

2.0部

7部

1.5部

1部

た。次いで温度を95℃に保ちながら下記単量体混合物を4時間滴下した。

【0077】

4.2部

1.2部

1.5部

3.0部

0.7部

0.15部と脱イオン水9.5部を仕込み、85℃に昇温

した。続いて下記の単量体混合物を水8.0部にホモキ

サーを用いて分散してから過硫酸アミン2.0部に

を添加した。その水分散液を5時間かけてフラスコ中に

滴下し、さらに2時間加熱させて不揮発分3.9%の乳白

色のエマルションを得た。得られたエマルションは脱イ

オン水で不揮発分1.0%に希釈して性能試験に用いた。

【0079】

2.5部

50.5部

3部

1部

20部

8.7部

この脱イオン水の水滴を形成し、水滴の接触角を協和化

字社製コンタクトアンゲルメーターDCCA型にて測定し

た。接触角の数値が大きい程親水性良好であることを示

す。

【0082】(*3) 耐水性：各塗装板を20℃の上水

に6時間浸水した後、塗面に異常のないものを○、白化

やフクレが認められるものを×とした。

【0083】

【表1】

表1

比較例	実施例										塗膜外観	撥水性(°)	耐水性
	1	2	3	4	5	6	7	8	9	10			
×	○	○	○	○	○	○	○	○	○	○	×	77	×
×	○	○	○	○	○	○	○	○	○	○	×	65	×
×	○	○	○	○	○	○	○	○	○	○	×	77	×

【0084】水性塗料の作成

実施例10

実施例1において、滴下する単量体混合物として下記の

単量体混合物を用いた以外は実施例1と同様にして行

た。

【0085】

なり、このシラノール基が水溶性もしくは水分散性を著

しく向上させるために克服でき、しかも水溶性/水分散

性を付与する官能基を有する単量体(c)の共重合量を

少なくすることが可能となり親水性を向上させることが

できる。また該共重合体水溶液もしくは水分散液による

塗膜の乾燥過程においては、シラノール基同士が自己凝

合反応により強固な架橋構造を形成するため、良好な耐

水性を示す塗膜が得られる。

【0087】従って本発明の共重合体水溶液もしくは水

分散液をビニル成分として用いた水性塗料組成物は、

親水性及び耐水性に優れた塗膜を形成することができ

る。

【0086】

【作用及び発明の効果】本発明の共重合体水溶液もしく

は水分散液では、単量体(a)により導入された親水性

基による水溶性、水分散の難しさを、単量体(b)を共

重合成分とすることで共重合体中に導入されたアルコキ

シシリル基が水の存在下で加水分解してシラノール基と

フロントページの続き

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(54) METHOD FOR PRODUCING FLUORINE-CONTAINING ACRYL COPOLYMER AQUEOUS EMULSION
AND COMPOSITION THEREFOR

(57)Abstract:

PURPOSE: To produce the subject emulsion having excellent water-repellency, oil repellency and stability by emulsifying a perfluoroalkyl acrylate monomer and an α,β -ethylenic unsaturated monomer and subsequently radically copolymerizing the mixture.

CONSTITUTION: (A) 2-40mol.% of a 6-12C alkyl group-containing perfluoroalkyl acrylate monomer, (B) 0.1-15mol.% of a carboxyl group-containing α,β -ethylenic unsaturated monomer copolymerizable with the component A, (C) 0-25mol.% of a hydroxyl group-containing α,β -ethylenic unsaturated monomer

copolymerizable with the components A and B, and (D) some other α,β -ethylenic unsaturated monomer

copolymerizable with the components A, B and C are emulsified in water in the presence of a surfactant. The

emulsion is preferably subjected to an ultrasonic wave-radiating treatment or to a high pressure homogenizing

treatment to minimize the emulsion particles into diameters of $\leq 0.3\mu$ (preferably 0.3-0.05 μ), followed by radically

polymerizing the particles to provide the objective emulsion.

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CLAIMS

[Claim(s)]

[Claim 1] (A) A perfluoroalkyl acrylate system monomer which has an alkyl group of the carbon numbers 6-12 2-40-mol% alpha which has (B) above (A) and a copolymerizable carboxyl group, beta-ethylenic unsaturated monomer 0.1-15-mol% (C) above (A), (B), alpha which has copolymerizable hydroxyl, beta-ethylenic unsaturated monomer 0-25-mol% (D) above (A), (B), (C), alpha other than the copolymerizable above, beta-ethylenic unsaturated monomer Emulsification dispersion of the 97.9-45-mol% is under water carried out using a surface-active agent, A manufacturing method of a fluorine-containing acrylic copolymer aqueous emulsion carrying out a radical polymerization after making particle diameter of a particulate material with a particle of 0.3 micrometer or less [Claim 2] A manufacturing method of a fluorine-containing acrylic copolymer aqueous emulsion indicated to claim 1 which sets particle diameter of a particulate material to 0.3 micrometer or less by ultrasonic irradiation or high voltage HOJINAIZA processing after carrying out emulsification dispersion of the monomer under water using a surface-active agent.

[Claim 3] (A) A manufacturing method of a fluorine-containing acrylic copolymer aqueous emulsion indicated to claim 1 or 2 whose perfluoroalkyl acrylate system monomer which has an alkyl group of the carbon numbers 6-12 is beta-(perfluoro octyl) ethyl acrylate [Claim 4] alpha which has a perfluoroalkyl acrylate system monomer which has an alkyl group of the carbon numbers 6-12, and a copolymerizable carboxyl group, A manufacturing method of a fluorine-containing acrylic copolymer aqueous emulsion with which beta-ethylenic unsaturated monomer was indicated in any 1 paragraph of claims 1 thru/or 3 which are acrylic acid [Claim 5] An aqueous emulsion of fluorine-containing acrylic copolymer particles which consist of a particulate material with a particle diameter of 0.3 micrometer - 0.05 micrometer manufactured by a method indicated in any 1 paragraph of claims 1 thru/or 4. [Claim 6] An aqueous composition which uses a hardenability compound as a basic component, comprising: An aqueous emulsion of fluorine-containing acrylic copolymer particles indicated in claim 5 paragraph. A basis reacted to these particles.

[Claim 7] An aqueous composition which uses as a basic component an aqueous emulsion of fluorine-containing acrylic copolymer particles indicated to claim 5, and a synthetic resin aqueous emulsion whose particle diameter of a particulate material is 0.1-10 micrometers.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]** which distributed this invention to the hyphdrogamy inside of the body Aquosity and ** it is related with the manufacturing method of the fluorine-containing (meta) acrylic (methacrylic system and acrylic are collectively written as acrylic) copolymer aqueous emulsion excellent in oiliness, and its constituent.

[0002]

[Description of the Prior Art] Resin containing fluoride is **, **** Oiliness's being shown and an antifoaming effect excellent in heat-resistant chemical resistance are used for a textile processing agent, adhesives, a paper coating agent, etc. from large reasons. Since it is rich in long-term weatherability in recent years, the use is considered also in the paint industry.

[0003] In the method of manufacturing resin containing these fluoride. Although there are a method of polymerizing fluorination olefin system monomers, such as a tetrafluoro olefin, a trifluoro olefin, and vinylidene fluoride, and alpha containing a fluoro alkyl group and the method of polymerizing beta-ethylenic unsaturated monomer. At ordinary temperature, since the former is a gaseous monomer, it has the inconvenience which must polymerize in high voltage. Therefore, it is used for manufacture of alpha containing the latter fluoro alkyl group, and the resin in which beta-ethylenic unsaturated monomer contains fluoride in the ordinary pressure polymerization.

[0004] As alpha containing a fluoro alkyl group, and a beta-ethylenic unsaturated monomer, fluoro alkyl acrylate and fluoro alkyl methacrylate (an acrylate monomer and a methacrylate monomer are collectively written as an acrylate system monomer) are usually used. However, since the price of this monomer is very high, to make character peculiar to fluoride give resin by a little use as much as possible is desired. ** of the resin film which contains a fluoro alkyl group on the other hand **** It is said that oiliness is revealed when a fluoro alkyl group arranges tidly to the air side in an interface, and it is known that the long-chain FURORO alkyl group is more effective. However, since a fluoro alkyl group has crystallinity, if chain length becomes too much long, since it will become a solid monomer at ordinary temperature and will not dissolve in other solvents, the perfluoroalkyl acrylate system monomer which has an alkyl group of the carbon numbers 6-12 is used ordinarily.

[0005] An emulsion [supply / the polymerization method of a monomer and / or resin] through environment or the safety of a human body to water is desired. However, The solubility of water HE of a perfluoroalkyl acrylate system monomer which has an alkyl group of the carbon numbers 6-12 with the usual emulsion polymerization method by which a monomer is supplied to the place (particles) of a reaction via the aqueous phase since it is very small. It was difficult to obtain the resin emulsion containing a fluoro alkyl group. Therefore, the special method has been proposed.

[0006] For example, a U.S. Pat. No. 3062765 item mixes with water the hydrophilic organic solvent in which the

methacrylate system monomer which has a fluoro alkyl group may be dissolved, and tries to perform an emulsion polymerization by increasing the solubility of the monomer to the aqueous phase. However, in this method, since comparatively a lot of hydrophilic organic solvents were required, the problem of environment or the safety of human body HE was not able to be solved. Since a hydrophilic organic solvent is included, in order for a problem to remain in the stability of an emulsion and to improve stability, the tendency for the water resisting property of the film which used the special fluorochemical surfactant, or the fizz of the emulsion occurred when making the amount of the surface-active agent used increase, or was obtained to get worse is large. Thus, since it was difficult to obtain the resin emulsion which contains a fluoro alkyl group according to an emulsion polymerization only through water, in the invention indicated to JP,2-147601,A. After adding water to the organic solvent solution of resin containing the fluoro alkyl group which carried out the radical polymerization and carrying out self-distribution in an organic solvent, the resin emulsion which makes an organic medium distill off and contains a fluoro alkyl group has been obtained.

[0007]

[Problem(s) to be Solved by the Invention]The good method of obtaining the resin emulsion which carries out the radical polymerization of the acrylate system monomer which has a poorly soluble fluoro alkyl group to water directly by the aqueous phase, and contains a fluoro alkyl group with sufficient stability did not have the former.

[0008]

[Means for Solving the Problem]After distributing under water a monomer composition which contains a perfluoroalkyl acrylate system monomer which has an alkyl group of the carbon numbers 6-12 as a result of this invention persons' repeating research wholeheartedly and creating a monomer pre emulsion, After particle diameter of this pre emulsion was 0.3 micrometer or less by ultrasonic irradiation or high pressure homogenizer treatment, when a radical polymerization was performed, it found out that a resin emulsion containing a stable fluoro alkyl group could be obtained.

[0009]That is, alpha in which this invention has a copolymerizable carboxyl group with "(perfluoroalkyl acrylate system monomer 2-40mol% (B which has alkyl group of 1) and (A) carbon numbers 6-12) above (A), beta-ethylenic unsaturated monomer 0.1-15-mol% (C) above (A), (B), alpha which has copolymerizable hydroxyl, beta-ethylenic unsaturated monomer 0-25-mol% (D) above (A), (B), (C), alpha other than the copolymerizable above, beta-ethylenic unsaturated monomer Emulsification dispersion of the 97.9-45-mol% is under water carried out using a surface-active agent, Manufacturing method (2) of a fluoroine-containing acrylic copolymer aqueous emulsion carrying out a radical polymerization after making particle diameter of a particulate material with a particle of 0.3 micrometer or less After carrying out emulsification dispersion of the monomer under water using a surface-active agent, A manufacturing method of a fluoroine-containing acrylic copolymer aqueous emulsion indicated to claim 1 which sets particle diameter of a particulate material to 0.3 micrometer or less by ultrasonic irradiation or high voltage HOJINAIZA processing.

(3) An alkyl group of the (A) carbon numbers 6-12. Manufacturing method (4) of a fluoroine-containing acrylic copolymer aqueous emulsion indicated to claim 1 or 2 whose perfluoroalkyl acrylate system monomer which it has is beta-(perfluoro octyl) ethyl acrylate An alkyl group of the carbon numbers 6-12, alpha which has a perfluoroalkyl acrylate system monomer which it has, and a copolymerizable carboxyl group, beta-ethylenic unsaturated monomer by a method indicated in any 1 paragraph of manufacturing method (5) claims 1 thru/or 4 of a fluoroine-containing acrylic copolymer aqueous emulsion indicated in any 1 paragraph of claims 1 thru/or 3 which are acrylic acid. An aqueous emulsion of fluoroine-containing acrylic copolymer particles which consist of a particulate material with a particle diameter of 0.3 micrometer - 0.05 micrometer manufactured.

(6) An aqueous composition which uses as a basic component an aqueous emulsion of fluoroine-containing acrylic copolymer particles indicated in claim 5 paragraph, and a hardenability compound which has a basis reacted to these particles.

(7) Aqueous composition which uses as a basic component an aqueous emulsion of fluorene-containing acrylic copolymer particles indicated to claim 5, and a synthetic resin aqueous emulsion whose particle diameter of a particulate material is 0.1-10 micrometers. "

It is alike and is related.

[0010] If it is made to only emulsify underwater like the usual emulsion polymerization, since hydrophobicity is large, the monomer which has a perfluoroalkyl group cannot enter easily into micell, and cannot form an emulsion of a monomer. So, this invention dissolves a monomer which has a perfluoroalkyl group in other monomers, and distributes this mixture in water using a surface-active agent. However, since particle diameter of a particulate material is too large now again, still smaller particles must be distributed. If it is not made to distribute guttate very small, it will be generated so much by gelling thing during a polymerization, and the feature of a fluorene-containing acrylic copolymer is hardly observed in an emulsion portion excluding a stable emulsion polymerization not only not being performed but a gelling thing. It is necessary to make it at least 0.3 micrometer or less. In order to distribute a very small drop, it is preferred to irradiate with an ultrasonic wave or to distribute with a high voltage homogenizer etc. Of course, law may both be suitably used together, for example, high pressure homogenizer treatment may be carried out, and ultrasonic irradiation may be carried out further.

[0011] In this way, a method of carrying out the radical polymerization of the obtained monomer pre emulsion within particles directly is learned as a mini emulsion polymerization method, and that particle diameter of a monomer pre emulsion is grains of 0.5 micrometer or less and for the particle to be stable and not to break during a polymerization are needed. Thus, in order to perform stable mini emulsion polymerization, it is known that higher alcohol and hexadecane are effective and higher alcohol is not used as emulsion stabilizer, it will have been supposed that an emulsification system will collapse during a polymerization. This was the common sense of mini emulsion polymerization.

[0012] However, even if it does not add an emulsification stable auxiliary agent, mini emulsion polymerization advances stably, an acrylic system monomer or a polymer which has a perfluoroalkyl group which is accepted with - - emulsion polymerization method does not deposit, or a gelling thing does not generate a method in particular of this invention so much. This invention person thinks that the acrylic system monomer itself which has a perfluoroalkyl group has contributed to the stability of a monomer pre emulsion.

[0013] As a perfluoroalkyl acrylic system monomer which has an alkyl group of the (A) carbon numbers 6-12 used for this invention, for example, $\text{CH}_2=\text{CHCO}_2\text{C}_6\text{H}_{13}$, $\text{CH}_2=\text{CHCO}_2\text{C}_8\text{H}_{17}$, $\text{CH}_2=\text{CHCO}_2\text{C}_6\text{H}_{13}$, $\text{CH}_2=\text{CHCO}_2\text{C}_8\text{H}_{17}$, $\text{CH}_2=\text{CHCO}_2\text{C}_{10}\text{H}_{21}$, $\text{CH}_2=\text{CHCO}_2\text{C}_{12}\text{H}_{25}$, $\text{CH}_2=\text{CHCO}_2\text{C}_{10}\text{H}_{21}$, $\text{CH}_2=\text{CHCO}_2\text{C}_{12}\text{H}_{25}$, etc. are mentioned. In particular, $\text{CH}_2=\text{CHCO}_2\text{C}_6\text{H}_{13}$, $\text{CH}_2=\text{CHCO}_2\text{C}_8\text{H}_{17}$, $\text{CH}_2=\text{CHCO}_2\text{C}_{10}\text{H}_{21}$, $\text{CH}_2=\text{CHCO}_2\text{C}_{12}\text{H}_{25}$ (beta-perfluoro octyl) ethyl acrylate) is preferred.

[0014] The amount of perfluoroalkyl acrylic system monomer used which has an alkyl group of the carbon numbers 6-12 is 2-40-mol%, and is 5-20-mol% preferably. There is no effect of a perfluoroalkyl group less than [2mol%], and it is **. Aqueosity is not acquired. If 40-mol% is exceeded and a fluorochemical surfactant will not be used so much, it becomes impossible to create a pre emulsion with fine particle diameter, and an emulsion obtained by carrying out in this way has a bad water resisting property, it turns into an emulsion to which it is easy to foam, and has a not desirable fault.

[0015] Alpha which has a perfluoroalkyl acrylic system monomer which has an alkyl group of the carbon numbers 6-12 used for this invention, and a copolymerizable carboxyl group, As a beta-ethylenic unsaturated monomer, acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic acid half ester, butelic acid half ester, itaconic acid half ester, etc. are mentioned. ** where the effect nearly exertion of the perfluoroalkyl group was carried out and which an emulsion polymerization is not only stably performed by using alpha which has a

carboxyl group, and beta-ethylenic unsaturated monomer, but was excellent Aquosily is acquired.

[0016](B) The amount of alpha which has a carboxyl group, and beta-ethylenic unsaturated monomer used is 0.1-15-mol%, and is 2.5-10-mol% preferably. As for the stability of an obtained emulsion, less than [0.1mol%] is insufficient, and since it paint-izes or is generated by gelling thing during preservation, it is not desirable. When 15-mol% is exceeded, there is a fault of the water resisting property of a coat falling.

[0017](C) alpha which has a perfluoroalkyl acrylate monomer which has an alkyl group of the aforementioned (A) carbon numbers 6-12 used for this invention, and the (B) carboxyl group, As beta-ethylenic unsaturated monomer, and alpha which has copolymerizable hydroxyl and beta-ethylenic unsaturated monomer, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxypropyl methacrylate, 1,4-butylene-glycol monoacrylate, hydroxystyrene, 2-hydroxybutyl methacrylate, 2-hydroxy-3-phenoxypolyacrylate, etc. are mentioned.

[0018]A compatible isomer like acetoxetoxyethylmethacrylate and acetoxetoxyethyl acrylate as a special monomer can be used also with the enol form or keto form. alpha which has hydroxyl, and especially beta-ethylenic unsaturated monomer are ** more, when alpha which has hydroxyl, and beta-ethylenic unsaturated monomer are used, although it is not necessary to use it. Aquosily improves, hydroxyl turns into a reaction group in a constituent which used especially a hardening reaction compound together, and a hardening reaction is fully performed. The amount of alpha which has hydroxyl, and beta-ethylenic unsaturated monomer used is 0-25-mol%, and is 5-15-mol% preferably. If 25-mol% is exceeded, a coat after hardening becomes weak and is not preferred. As the above (A) used for this invention, (B), the (C) monomer, and alpha except [copolymerizable] said and beta-ethylenic unsaturated monomer, Vinyl acetate, butanoic acid vinyl, vinyl propionate, vinyl ester of carboxylic acid which branched by an alpha position, Which vinyl ester, Methyl acrylate, ethyl acrylate, butyl acrylate, Acrylic ester, such as acrylic acid 2 ethylhexyl one; Methyl methacrylate, Unsaturated acid ester, such as methacrylic-acid-ester, dibutyl maleates, such as ethyl methacrylate, butyl methacrylate, and methacrylic acid 2 ethylhexyl one, and fumaric acid dibutyl, styrene and acrylonitrile; etc. are mentioned.

[0019]It can also be used transposing a part of these monomers to functionality or a cross-linking monomer. As functionality or a cross-linking monomer, acrylamide, N-methylolacrylamide, glycidyl methacrylate, divinylbenzene, triallyl isocyanurate, tetra allyloxy ethane, etc. are mentioned. Fluoride content divinyl compounds, such as 1,4-divinyl perfluoro n-butane and 1,6-divinyl perfluoro n-hexane, can also be used for a cross linking agent.

[0020]The amount of (A), (B), the (C) monomer, and alpha used except [copolymerizable] said and beta-ethylenic unsaturated monomer is the remaining quantity excluding the amount of (A), (B), and the (C) monomer used from the monomer whole quantity, and is 97.9 - 45-mol% of the range. It enabled an aqueous emulsion not to use a solvent but to manufacture a fluorine-containing acrylic copolymer directly by a drainage system by this invention.

[0021]A fluorine-containing acrylic copolymer aqueous emulsion composition obtained by this invention is ** by drying. Aquosily, ** A coat excellent in oiliness is formed and it excels in heat resistance, weatherability, lightfastness, chemical resistance, a mold-release characteristic, slide nature, etc. Therefore, a synthetic resin aqueous emulsion can use it for a binder for paints, a textiles processing agent, a paper coating agent, cement admixture, adhesives, etc. which are generally applied useful. In particular, it is ** of a coat. Aquosily, ** A surface coating agent using oiliness is useful, and as a coating base material, it can be used for a thing of wide ranges, such as a textiles substance, a nonwoven fabric, paper, leather, rubber, wood, metal, gypsum fibrous, an ALC panel, asphalt, glass, glass fiber, pottery, and a plastic, especially is not limited.

[0022]As a fluorine-containing acrylic copolymer aqueous emulsion composition obtained by this invention, especially when solvent resistance is searched for further, it is preferred to blend a hardening reaction compound

with a fluorene-containing acrylic copolymer aqueous emulsion obtained by this invention. It is the method of

making it heat-harden using a blocking isocyanate preferably especially, and solvent resistance of a film produced by carrying out in this way improves remarkably. It is preferred to use alpha which has hydroxyl, and beta-ethylenic unsaturated monomer especially as a monomer composition for manufacturing a fluorene-containing acrylic copolymer aqueous emulsion in a case of using together with a hardening reaction compound. A

hardening compound reacts to this hydroxyl. If other functional groups, for example, a carboxyl group, an amino group, etc. are made to contain, of course, it will harden similarly, a compound which reacts to hydroxyl as a hardening reaction compound — that is, Thermosetting resin, such as melamine resin, an epoxy resin, and phenol resin; a blocking isocyanate is the most preferred although a compound etc. which have an isocyanate

compound, a diethylene urea derivative, a blocking isocyanate, and two or more epoxy groups are used. Although the amount in particular of hardening reaction compound used is not limited, it is one to 20 weight section to solid content 100 weight section of a fluorene-containing acrylic copolymer aqueous emulsion.

[0023] A fluorene-containing acrylic copolymer aqueous emulsion of this invention can be used mixing it with a

synthetic resin aqueous emulsion. As an aqoustly synthetic resin emulsion to blend, what is necessary is just an aqoustly synthetic resin emulsion conventionally used for a binder for paints, a textiles processing agent, a binder for paper coating, adhesives, etc., and a synthetic rubber emulsion is also contained. Specifically A vinyl acetate

system resin aqueous emulsion, a styrene resin aqueous emulsion, An acrylic resin aqueous emulsion, ethylene and a vinyl acetate system resin aqueous emulsion, Ethylene and a VCM/PVC system resin aqueous emulsion, a vinyl acetate acrylic resin aqueous emulsion, A vinyl acetate BEOBA (shell chemicals company, registered trademark) system resin aqueous emulsion, Although rubber RATTOKUSU, such as thermoplastics aqueous

emulsions, such as a styrene acrylic resin aqueous emulsion, styrene-butadiene rubber latex, styrene butadiene acrylonitrile rubber latex, and polyisoprene rubber latex, is raised, In addition, a proper emulsion can be used. These aqueous emulsions are manufactured by the usual emulsion polymerization using a surface-active agent or protective colloid, and particle diameter is 0.1-10 micrometers. A rate to blend changes with purposes, and

although not limited, it is used for ten to fluorene-containing acrylic copolymer aqueous emulsion 99 weight section (solid content conversion) by 90 to aqueous emulsion 1 usual weight section (solid content conversion). A

fluorene-containing acrylic copolymer aqueous emulsion is ** to a coat at ten or less weight sections. there are few effects of giving aqoustly, it is unchanging with 100 weight sections in 99 or more weight sections, and an effect of adding the usual aqueous emulsion is not acquired. ** of a coat in order to fully maintain aqoustly and to raise

mechanical properties, such as the adhesion of substrate HE of a coat, intensity, ductility of a coat, 50 to fluorene-containing acrylic copolymer aqueous emulsion 99 weight section (solid content conversion) and 50 to aqueous emulsion 1 usual weight section (solid content conversion) are preferred, and it is ** to a coat. They are some **

to a coat of an aqueous emulsion from which aqoustly is not acquired. If it is the purpose of giving aqoustly, the purpose can be enough reached by ten to fluorene-containing acrylic copolymer aqueous emulsion 50 weight section in 90 to aqueous emulsion 50 usual weight section (solid content conversion).

[0024] According to the purpose, a thickener, a plasticizer, a defoaming agent, paints, colorant, a bulking agent, a perfume, an antiseptic, a fluorescent brightener, an antioxidant, an ultraviolet ray absorbent, a reinforcing agent, a spray for preventing static electricity, an anti-blocking agent, fire retardant, lubricant, a tackifier, etc. can be

blended with an aqueous composition of this invention. In order to raise especially viscosity of an aqueous composition, it is preferred to blend water soluble polymer compounds, such as polyvinyl alcohol, polyacrylate, water-soluble starch, and a water soluble cellulose derivative, as a thickener.

[0025]

[Example] Next, an example is given and this invention is explained concretely.

[0026] Weighing of 8.3 g (5-mol%) of example 1 beta-(perfluoro octyl) ethyl acrylate, 40.6 g (90-mol%) of n-butyl methacrylate, and the 80% acrylic acid 1.5g (5-mol%) was carried out to the Erlenmeyer flask, and it was

considered as uniform monomer mixed liquor. Add 2.5 (polyoxyethylene-alkyl-phenyl-ether sodium sulfate) g and the surface-active agent solution which comprises 48g of 0.25g of phosphoric acid disodium and 12 monohydrate deionized water to monomer mixed liquor, and it agitates with a magnet stirrer. The monomer pre emulsion with a mean particle diameter of about 1 micrometer was obtained. Then, when ultrasonic irradiation was performed for 60 minutes using the ultrasonic transmitter (W-210R Honda Electronics Co., Ltd.) of frequency 40KHZ, carrying out bubbling of the monomer pre emulsion by nitrogen gas, mean particle diameter fell to about 0.2 micrometer. In another container, the catalyst solution and the reducing agent solution were created as follows.

Catalyst solution Par butyl H69 (made by Nippon Oil & Fats Co., Ltd.) 0.73g Emulgen 911 (made by Kao Corp.) 0.25g deionized water 9.3 g Reducing agent solution Super light C(made by Mitsubishi Gas Chemical Co., Inc.) 0.5g deionized water 9.5g agitator, a reflux condenser, After carrying out temperature up of the reactor provided with the dropping funnel, the thermometer, and the nitrogen gas introducing pipe to 55 **, 20% was taught for the monomer pre emulsion which performed steamy ultrasonic irradiation, and 10% and 10% of the reducing agent solution of the catalyst solution were added. After adding 10% and 10% of the reducing agent solution of the catalyst solution further after 10-minute progress, the remaining monomer pre emulsions were dropped over about 3 hours more nearly continuously than a dropping funnel. In the meantime, the temperature in a reactor was held at 55-60 **, and divided and added 60% and 60% of the reducing agent solution of the catalyst solution every 15 minutes. After the end of dropping, 10% and 10% of the reducing agent solution of the catalyst solution were added further, it agitated for 1 hour, and the reaction was terminated. As a result, 43 % of the weight of concentration and the stable fluorine-containing acrylic copolymer aqueous emulsion of pH 2.2 were obtained. ** of the tunic which the mean particle diameter of this fluorine-containing acrylic copolymer aqueous emulsion is 0.2 micrometer, and is produced by carrying out spreading desiccation of this fluorine-containing acrylic copolymer aqueous emulsion at an aluminum plate ** whose hydrate is good at R9 Aqosity was shown.

The particle diameter of the test-method emulsion was measured using the diameter analyzer of product model made from Nicomp Instruments Inc. 370 submicron particle.

**Coating of the pH of the measurement fluorine-containing acrylic copolymer aqueous emulsion of hydrate was carried out to the aluminum plate with the wire rod of #40 after adjusting to 5-7 with sodium hydroxide solution 10%, and it dried at 80 **, was further neglected within the desiccator on about the 10th, and was considered as the sample. ** of the sample which carried out coating to the aluminum plate according to JIS.P8137 The examination length of 100 mm estimated hydrate. **JIS.P8137 performed the valuation basis of hydrate. In evaluation, the larger one [number] is ** more at R1 to R10. Aqosity is high.

[0027]After agitating and obtaining the pre emulsion of the monomer composition of Table 1 with a magnet stirrer by the same technique as example 2 Example 1, it processed once by pressure 8,000P.S.I. using the high voltage homogenizer (GAULIN INC. make MANTON GAOLIN LABORATORY HOMOGENIZER form 15M-6TA). By this processing, the mean particle diameter of the monomer pre emulsion was set to about 0.2 micrometer, and performed the same operation as Example 1 after that.

[0028]Using the monomer composition of the example 3 table 1, by the same operation as Example 1, the radical emulsion polymerization was performed and the fluorine-containing acrylic copolymer aqueous emulsion was obtained.

[0029]After adjusting pH to the fluorine-containing acrylic copolymer aqueous emulsion obtained in example 4 Example 3 by sodium hydroxide 5% 5-7, the diphenylmethanebis-4 of 23 % of the weight of active principles, 4'-N, 10phr **** and after mixing uniformly, coating of the N'-diethyleneurea aqueous dispersion liquid (made by Akihari chemical industry incorporated company) was carried out to the aluminum board, and it dried at 80 **. ***** was performed on condition of for [150 more **x] 30 minutes, hardening by an isolation isocyanate group was performed, and it cooled even to the room temperature. When the resistance to solvents test of the cured film was carried out by the rubbing test by toluene, 100 times was borne, solvent resistance was improving and the

heat-curing reaction was checked.

[0030] Using the monomer composition of the example 5 table 1, ultrasonic irradiation was performed for 120 minutes, except the mean particle diameter of the monomer pre emulsion having been about 0.1 micrometer, the radical emulsion polymerization was performed and the fluorine-containing acrylic copolymer aqueous emulsion was obtained by the same operation as Example 1.

[0031] After adjusting pH to the fluorine-containing acrylic copolymer aqueous emulsion obtained in example 6 Example 5 by sodium hydroxide 5% 5-7, the diphenylmethanebis-4 of 23 % of the weight of active principles, 4-N, 10phr **** and after mixing uniformly, coating of the N'-diethyleneurea aqueous dispersion liquid (made by Akina chemical industry incorporated company) was carried out to the aluminum board, and it dried at 80 **. It heat-treated on condition of for [150 more **x] 30 minutes, hardening by an isolation isocyanate group was performed, and it cooled even to the room temperature. When the resistance to solvents test of the cured film was carried out by the rubbing test by toluene, 100 times was borne, solvent resistance was improving and the heat-curing reaction was checked.

[0032] To fluorine-containing acrylic copolymer aqueous emulsion 80 weight section (solid content conversion) obtained in example 7 Example 3. Vinyl acetate (80) and dibutyl maleate (20) copolymer aqueous emulsion 20 weight section (solid content conversion) with a mean particle diameter of 1 micrometer produced by the usual emulsion polymerization by using polyvinyl alcohol as protective colloid was added, agitation mixing was carried out uniformly, and the aqueous composition was obtained. It is ** by the technique same about the obtained aqueous composition as Example 1. It is ** when aqueously was investigated. Hydrature was the same as that of Example 3 at R₁₀. When the aqueous composition was applied and dried at the glass plate, the coat was formed and adhesion power was investigated, as compared with the fluorine-containing acrylic copolymer emulsion independent obtained in Example 3, it was improving remarkably.

[0033] Fluorine-containing acrylic copolymer aqueous emulsion 30 weight section (solid content conversion) obtained in Example 3 to ethyl acrylate aqueous emulsion 70 weight section (solid content conversion) with a mean particle diameter of 0.5 micrometer produced by the usual emulsion polymerization by using example 8 surface-active agent as an emulsifier -- in addition, Agitation mixing was carried out uniformly and the aqueous composition was obtained. It is the technique same about the obtained aqueous composition as Example 1, and is **. It is ** when aqueously was investigated. Hydrature was the same as that of Example 3 at R₁₀. When the aqueous composition was applied and dried at the glass plate, the coat was formed and adhesion power was investigated, as compared with the fluorine-containing acrylic copolymer emulsion investigated, as compared with the fluorine-containing acrylic copolymer emulsion obtained in Example 3, it was improving remarkably.

[0034]

[Table 1]

実施例	条件									
	β-(1-β-オロキシル)エチルアクリレート	n-ブチルアクリレート	ト-ブチルアクリレート	2-エトキシエチルアクリレート	アクリル酸	マクロビニルモノマー攪拌後の粒子径μm (約)	超音波処理	○高圧ホモジナイザー	処理後の粒子径 μm (約)	重合温度
6	5	83			10	2	○		0.1	60
5	25	65			5	1	○		0.2	60
4	25	65			5	1	○		0.2	60
3	15	60	20		5	1		○	0.2	60
2	5	90			5	1	○		0.2	60
1	5	90			5	1	○		0.2	60
重合										
E m										
粘度 (%)										
粘度 (cP)										
pH										
重合安定性										
マクロビニルモノマー (phr)										
加水度										
トルエン・マクロビニルモノマー										

[0035]Except not ultrasonically in comparative example 1, when the radical polymerization was

performed completely like Example 1, it was generated so much by the gelling thing during the polymerization.

The emulsion containing a gelling thing is ****(ed) after the end of a polymerization, and it is ** by the same

technique as Example 1. It is ** when hydrate was investigated. Aqueously was not accepted.

[0036]without using beta-(perfluoro octyl) ethyl acrylate using the monomer composition of the comparative

example 2 table 2, it did not ultrasonicate, but by the same operation as the comparative example 1, the usual

radical emulsion polymerization was performed and the acrylic (meta-) copolymer aqueous emulsion was

obtained. It is ** by the technique same about the obtained acrylic (meta) copolymer aqueous emulsion after the

end of a polymerization as Example 1. It is ** when hydrate was investigated. Aqueously was not accepted.

[0037]It is beta-(perfluoro octyl) ethyl acrylate about the monomer mixed liquor used in comparative example 3

Example 1. 1mol% n-butyl methacrylate 94mol% acrylic acid The acrylic copolymer aqueous emulsion was

obtained like Example 1 except having considered it as 5-mol%. By the technique same about the obtained

acrylic copolymer aqueous emulsion as Example 1, it is **. It is ** when hydrate was investigated. Aqueously was

not accepted.

[0038]Except having used trifluoroethylmethacrylate instead of beta-(perfluoro octyl) ethyl acrylate using the

monomer composition of the comparative example 4 table 2, the radical emulsion polymerization as well as

Example 1 was performed, and the acrylic copolymer aqueous emulsion was obtained. It is ** by the technique

same about the obtained acrylic copolymer aqueous emulsion after the end of a polymerization as Example 1. It

is ** when hydrate was investigated. Aqueously was not accepted.

[0039]beta-(perfluoro stearyl) ethyl acrylate was used instead of beta-(perfluoro octyl) ethyl acrylate used in

comparative example 5 Example 1. beta-(perfluoro stearyl) ethyl acrylate did not dissolve in n-butyl methacrylate,

and even if it performed ultrasonic irradiation, a uniform monomer pre emulsion was not able to be obtained. An

aqueous emulsion was not able to be obtained even if it performed the radical emulsion polymerization.

[0040]

[Table 2]

		比較例				
		1	2	3	4	5
重合	β-(1-β-フルオロオクチル)エチルアクリレート	5	0	1		
	トリフルオロエチルアクリレート				5	
	β-(1-β-フルオロオクチル)エチルアクリレート					5
	α-アクリルアクリレート	90	95	94	90	90
	α-アクリルアクリレート					
	2-ヒドロキシエチルメタクリレート					
	アクリル酸	5	5	5	5	5
	アクリルメタクリレート-ラテックス後の粒子径μm (約)	1	1	1	1	X
	超音波処理				○	
	○高圧ホモジナイザー					
	処理後の粒子径μm (約)			0.2	0.2	X
	重合温度	60	60	60	60	
条件	重合時間	3	3	3	3	
	温度 (%)	—	—	—	43	43
	粘度 (cP)	—	—	—	<100	<100
	pH	—	—	—	2.2	2.2
	重合安定性	X	○	○	○	X
	フロック化インジケータ (phr)	--	--	--		
	攪拌度	R ₀	R ₀	R ₀	R ₀	R ₀
	トルエン・ラビソグラスト	--	--	--	--	--
Bm	攪拌度					
	トルエン・ラビソグラスト					
	攪拌度					
	トルエン・ラビソグラスト					
	攪拌度					
	トルエン・ラビソグラスト					
	攪拌度					
	トルエン・ラビソグラスト					
	攪拌度					
	トルエン・ラビソグラスト					
	攪拌度					
	トルエン・ラビソグラスト					

[0041]

[Effect of the invention] Stability and ** Aqueosity and ** The microparticulate fluoride content acrylic aqueous emulsion excellent in oiliness can be manufactured by dissolving a polymerization component in a monomer, distributing microparticulate underwater and polymerizing under water. And it is ** by using this emulsion composition alone or using together with other substances. Aqueosity and ** It can be used for the various application which needs oiliness.

[Translation done.]

METHOD FOR PRODUCING FLUORINE-CONTAINING ACRYL COPOLYMER
AQUEOUS EMULSION AND COMPOSITION THEREFOR

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New INPADOC patent family

Abstract of JP5017538

PURPOSE: To produce the subject emulsion having excellent water-repellency, oil repellency and stability by emulsifying a perfluoroalkyl acrylate monomer and an alpha,beta-ethylenic unsaturated monomer and subsequently radically copolymerizing the mixture. CONSTITUTION: (A) 2-40mol.% of a 6-12C alkyl group-having perfluoroalkyl acrylate monomer, (B) 0.1-15mol.% of a carboxyl group-containing alpha,beta-ethylenic unsaturated monomer copolymerizable with the component A, (C) 0-25mol.% of a hydroxyl group-containing alpha,beta-ethylenic unsaturated monomer copolymerizable with the components A, B and C, and (D) some other alpha,beta-ethylenic unsaturated monomer copolymerizable with the components A, B and C are emulsified in water in the presence of a surfactant. The emulsion is preferably subjected to an ultrasonic wave-radiating treatment or to a high pressure homogenizing treatment to minimize the emulsion particles into diameters of <=0.3mu (preferably 0.3-0.05mu), followed by radically polymerizing the particles to provide the objective emulsion.

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(54) 【発明の名称】 含フッ素アクリル系共重合体水性エマルジョンの製造方法及びその組成物

(57) 【要約】
【目的】 ▲撥水性と▲撥油性及び安定性に優れた、微粒子状の含フッ素アクリル共重合体水性エマルジョンの製造方法と、得られたエマルジョンおよび他の物質との混合物を提供する。
【構成】 炭素数6〜12のアシル基を有するパーロオロアクリレートと、共重合可能なカルボキシル基含有α、β-エチレン性不飽和単量体と、共重合可能なヒドロキシル基含有α、β-エチレン性不飽和単量体と、その他の共重合可能なα、β-エチレン性不飽和単量体を、界面活性剤を用いて水中に乳化分散させ、粒径を0.3μm以下の粒子としてから重合してエマルジョンを製造する。得られたエマルジョンはそのまま使用するか他の物質と混合して使用する。

【特許請求の範囲】

【請求項1】 (A)炭素数6～12のアルキル基を有する1-アルコキシアルキルアクリレート系単量体

～40mol%

(B)上記(A)と共重合可能なカルボキシアルキル基を有する α 、 β -エチレン性

不飽和単量体

(C)上記(A)、(B)と共重合可能なヒドロキシアルキル基を有する α 、 β -エ

チレン性不飽和単量体

(D)上記(A)、(B)、(C)と共重合可能な上記以外の α 、 β -エチレ

97.9～45mol%

【従来の技術】 フッ素を含有する樹脂は、▲線▼水▲線▼油性を示すこと、耐熱耐薬品性に優れている防汚効果が大い等の理由から、繊維加工剤、接着剤、紙加工剤等に利用されてきた。又、近年は長期の耐候性に富むことから、塗料業界でもその利用を考えている。

【0003】 これらフッ素を含有する樹脂を製造する方法には、チトアルコキシアルキル、トリアルコキシアルキル、フッ化ビニリデンなどのフッ化アルキル系単量体を重合する方法と、アルコキシアルキル基を含有する α 、 β -エチレン性不飽和単量体を重合する方法とが、前者は常温では気体の単量体であるために高圧で重合しなければならない不便がある。従って、常圧で重合し得るアルコキシアルキル基を含有する α 、 β -エチレン性不飽和単量体がフッ素を含有する樹脂の製造に用いられている。

【0004】 アルコキシアルキル基を含有する α 、 β -エチレン性不飽和単量体としては、アルコキシアルキルアクリレートやアルコキシアルキルメタクリレート（アクリレート単量体とメタクリレート単量体を併せてアクリレート単量体と略記する）が普通用いられている。しか

し、この単量体の価格が非常に高いため、出来るだけ少量の使用でフッ素特有の性質を樹脂に付与させることが望まれている。又、一方アルコキシアルキル基を含有する樹脂アクリルムの▲線▼水▲線▼油性は界面において空気側にアルコキシアルキル基が優先的に配列することによって現れるとされ、長鎖のアルコキシアルキル基の方が効果的であることが知られている。しかし、アルコキシアルキル基は結晶性を有するために融点が高まりに長くなる。常温で固体の単量体となり、他の溶剤に溶解しなく、なることから、炭素数6～12のアルキル基を有するアルコキシアルキルアクリレート系単量体が普通に用いられている。

【0005】 単量体の重合方法及び樹脂の供給は環境や人体の安全性から水を媒体としたエマルジョンが望まれ、アルコキシアルキルアクリレート系単量体の水への溶解度は極めて小さいことから水相を経由して反応の場（粒子）へ単量体が供給される通常の乳化重合法によってアルコキシアルキル基を含有する樹脂エマルジョンを得ることは困難であった。そのために特殊な方法が提案さ

を界面活性剤を用いて水中に乳化分散させ、分散粒子の粒径を0.3 μ m以下の微粒となしからラジカル重合することを特徴とする含フッ素アクリル系共重合体水性エマルジョンの製造方法

【請求項2】 単量体を界面活性剤を用いて水中に乳化分散させた後、超音波照射または高圧ホジナイザー処理により分散粒子の粒径を0.3 μ m以下とする請求項1に記載された、含フッ素アクリル系共重合体水性エマル

ジョンの製造方法。

【請求項3】 (A)炭素数6～12のアルキル基を有する1-アルコキシアルキルアクリレート系単量体が β -（1-アルコキシアルキル）エチルアクリレートである請求項1または2に記載された含フッ素アクリル系共重合体水性エマルジョンの製造方法

【請求項4】 炭素数6～12のアルキル基を有する1-アルコキシアルキルアクリレート系単量体と共重合可能なカルボキシアルキル基を有する α 、 β -エチレン性不飽和単量体がアクリル酸である請求項1ないし3のいずれか1項に記載された含フッ素アクリル系共重合体水性エマル

ジョンの製造方法

【請求項5】 請求項1ないし4のいずれか1項に記載された方法により製造された粒径0.3 μ m～0.05 μ mの分散粒子からなる含フッ素アクリル系共重合体微粒子の水性エマルジョン。

【請求項6】 請求項5項に記載された含フッ素アクリル系共重合体微粒子の水性エマルジョンと、微粒子と反応する基を有する硬化性化合物とを主要成分とする水性組成物。

【請求項7】 請求項5項に記載された含フッ素アクリル系共重合体微粒子の水性エマルジョンと分散粒子の粒径が0.1～10 μ mである合成樹脂水性エマルジョンとを主要成分とする水性組成物。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は水媒体中に分散した▲線▼水性と▲線▼油性に優れた含フッ素（メタ）アクリル系（メタ）アクリル系およびアクリル系を併せてアクリル系と略記する）共重合体水性エマルジョンの製造方法及びその組成物に関する。

【0002】

＊ている。

【0007】

【発明が解決しようとする課題】水に難溶性のアルキルエステル系単量体を水相で直接ラジカル重合させ、安定性の良いアルキルエステル系単量体を含む樹脂エマルジョンを得る良い方法は従来なかった。

【0008】

【課題を解決するための手段】本発明者は鋭意研究を重ねた結果、炭素数6～12のアルキル基を有するパーフルオロアルキルエステル系単量体を含む樹脂エマルジョンを作成し、超音波照射あるいは高圧ホモジナイザ処理等により微細なエマルジョンの粒子径を0.3μm以下にしてからラジカル重合を行うと安定なアルキルエステル系単量体を含む樹脂エマルジョンを得られることを見いだした。

【0009】つまり、本発明は、

「(1) 炭素数6～12のアルキル基を有するパーフルオロアルキルエステル系単量体 2～40m

(B) 上記(A)と共重合可能なカルボキシ基を有するα、β-エチレン性 0.1～15m 0.1%

(C) 上記(A)、(B)と共重合可能なヒドロキシ基を有するα、β-エチレン性不飽和単量体 0～25m 0.1%

(D) 上記(A)、(B)、(C)と共重合可能な上記以外のα、β-エチレン性不飽和単量体 97.9～45m 0.1%

微粒子からなる含フッ素アルキル系共重合体微粒子の水 性エマルジョン。

(6) 請求項5項に記載された含フッ素アルキル系共重合体微粒子の水性エマルジョンと、陰微粒子と反応する基を有する硬化性化合物とを主要成分とする水性組成物。

(7) 請求項5項に記載された含フッ素アルキル系共重合体微粒子の水性エマルジョンと分散粒子の粒子径が0.1～10μmである合成樹脂水性エマルジョンとを主要成分とする水性組成物。」

【0010】通常の乳化重合のように単に水中に乳化させると、パーフルオロアルキル基を有する単量体は疎水性が大きいのでミセルの中に入り難く、モノマーのエマルジョンが形成出来ない。それ故本発明は、パーフルオロアルキル基を有する単量体を他のモノマーに溶解してこの混合物を界面活性剤を用いて水に分散する。しかし、これではまた分散粒子の粒径が大きすぎるので、更に小さい粒子に分散させなければならぬ。微少滴状に分散させないと重合中にゲル化物が多量に発生し、安定な乳化重合が行われなばかりか、ゲル化物を除いた、エマルジョン部分にはほとんど含フッ素アルキル系共重合体

れてきた。

【0006】例えば、米国特許3062765号は、フ

ルオロアルキル基を有するメタクリレート系単量体を溶解させ得る親水性有機溶媒に水に溶解し、水相への単量体の溶解度を増すことによって乳化重合を行うおとするものである。しかし、この方法では、比較的多量の親水性有機溶媒が必要ことから環境や人体への安全性の問題が解決できなかった。また親水性有機溶媒を含むことからエマルジョンの安定性に問題が残る、安定性を改良するために特殊なフッ素系界面活性剤を用いたり、界面活性剤の使用量を増加せたりすれば、エマルジョンの発泡性が増したり得られたアルキルの耐水性が悪化する傾向が大きい。この様に、水だけを媒体にして乳化重合によりフルオロアルキル基を含む樹脂エマルジョンを得ることは困難であったため、特開平2-147601号に記載された発明では、有機溶媒中でラジカル重合したフルオロアルキル基を含む樹脂の有機溶剤溶液に水を加えて自己分散させた後、有機溶媒を留去させてフルオロアルキル基を含む樹脂エマルジョンを得＊

を界面活性剤を用いて水中に乳化分散させ、分散粒子の粒径を0.3μm以下の微粒となしてからラジカル重合

することを特徴とする含フッ素アルキル系共重合体水性エマルジョンの製造方法

(2) 単量体を界面活性剤を用いて水中に乳化分散させた後、超音波照射または高圧ホモジナイザ処理により分散粒子の粒径を0.3μm以下とする請求項1に記載された、含フッ素アルキル系共重合体水性エマルジョンの製造方法。

(3) (A) 炭素数6～12のアルキル基を有するパーフルオロアルキルエステル系単量体がβ-（パーフルオロオクチル）エチルアクリレートである請求項1

または2に記載された含フッ素アルキル系共重合体水性エマルジョンの製造方法

(4) 炭素数6～12のアルキル基を有するパーフルオロアルキルエステル系単量体と共重合可能なカルボキシ基を有するα、β-エチレン性不飽和単量体が

の製造方法

(5) 請求項1ないし4のいずれか1項に記載された方法により製造された粒径0.3μm～0.05μmの分

[illegible]

(ル) エサルアルアクリートの費用は、森林警察隊が
わが警察署と同様の職能によって樹木の管理を執
行すること、(メカ) アクリル系防水塗料はアル
ジウムを得た。樹脂製で、塗られた(メタ) アクリル
系防水塗料はアルミニウムについて、演習として同機
な事柄に力づくで、水陸の置入とて、水陸に浸

